"STUDIES IN THE FLUORANTHENE SERIES"

by

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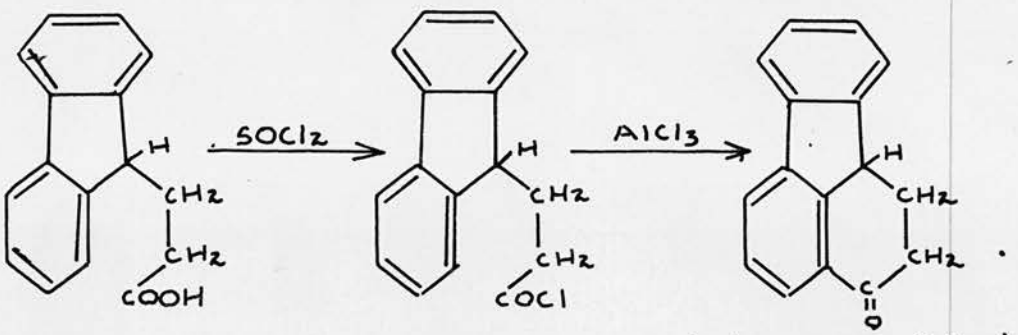
I N D E X.

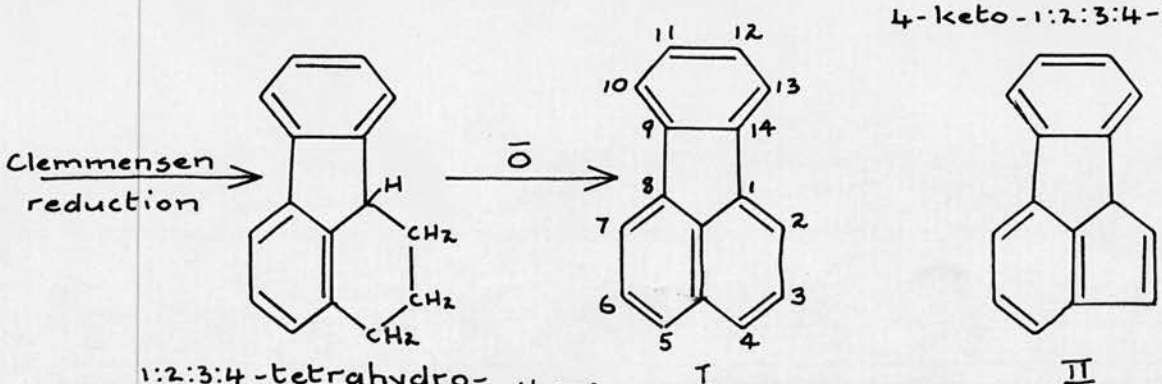
INTRODUCTION

This introduction gives an account of published work on the substitution of fluoranthene and the orientation of the substitution products. Syntheses of fluoranthene derivatives useful in orientation studies are described, but syntheses of other fluoranthene derivatives and of the fluoranthene itself have been omitted.

Until von Braun and Anton (Ber., 1929, 62, 145) synthesised fluoranthene and thus showed it to have the structure I, $C_{16}H_{10}$, the hydrocarbon was thought to have the formula $C_{15}H_{10}$, and the structure II. The synthesis gave 4-keto-1:2:3:4-tetrahydrofluoranthene and 1:2:3:4-tetrahydro-:fluoranthene, both important in orientation studies.



4-keto-1:2:3:4-tetrahydro-fluoranthene.



1:2:3:4-tetrahydro-fluoranthene.

I

II

Before the correct structure was known, some substitution products had been described, the hydrocarbon being called "idryl" in these early researches. Goldschmiedt (Ber., 1877, 10 2022) described a bromocompound but gave no melting point or analysis. Fittig and Gebhard (ibid, 1877, 10, 2141; Annalen, 1878, 193. 142.) prepared a dibromo-:compound and a trinitrocompound. A trichloro-:compound was described by Goldschmiedt (Wien. Akad Ber., (2 Abth) 81, 415; Monatsh., 1880, 1 221) and bromination of the hydrocarbon in acetic acid gave a tribromocompound M.P. >345°. Sulphonation gave a disulphonic acid, whose potassium salt upon fusion with potassium cyanide and subsequent heating with solid alkali gave a compound which was apparently an idryl monocarboxylic acid and not the expected dicarboxylic acid.

von Braun and Manz (Annalen, 1931, 488,111) showed that the work of Fittig (loc. cit.) and Goldschmiedt (loc. cit.) on dibromination, trinitration, and disulphonation could be reproduced although in the latter case some monosulphonic acid was also formed. They showed that if milder reaction conditions were used monosubstitution occurred and they made a detailed study of the three monosubstituted /

monosubstituted products and showed by conversion to common compounds that they all had the same orientation.

The monobromofluoranthene was converted to cyanofluoranthene by fusion with alkali cyanide, and subsequent hydrolysis gave fluoranthene carboxylic acid. $C_{16}H_9Br \longrightarrow C_{16}H_9CN \longrightarrow C_{16}H_9COOH$

Mononitrofluoranthene was reduced to the corresponding amine, which gave the phenol when heated with N.hydrochloric acid at 230°.

$$C_{16}H_9NO_2 \longrightarrow C_{16}H_9NH_2 \longrightarrow C_{16}H_9OH$$

Fluoranthene monosulphonic acid was converted to the sulphonyl chloride and the action of ethylamine on the latter gave fluoranthene sulpho-: ethylamide. Fluoranthene carboxylic acid was obtained by fusing the sulphoethylamide with alkali cyanide and hydrolysing the cyanofluoranthene thus formed. The acid chloride ethyl ester, and amide were prepared from the carboxylic acid. By heating the sulphoethylamide with caustic potash the phenol was produced and when heated with ethanolic ammonia this gave aminofluoranthene

$$C_{16}H_9SO_3H \longrightarrow C_{16}H_9SO_2Cl \longrightarrow C_{16}H_9SO_2NHEt$$

$$\downarrow$$

$$C_{16}H_9CN$$

$$\downarrow$$

$$C_{16}H_9COOH$$

$$\downarrow$$

$$C_{16}H_9COCl$$

$$\downarrow$$

$$C_{16}H_9CONH_2$$

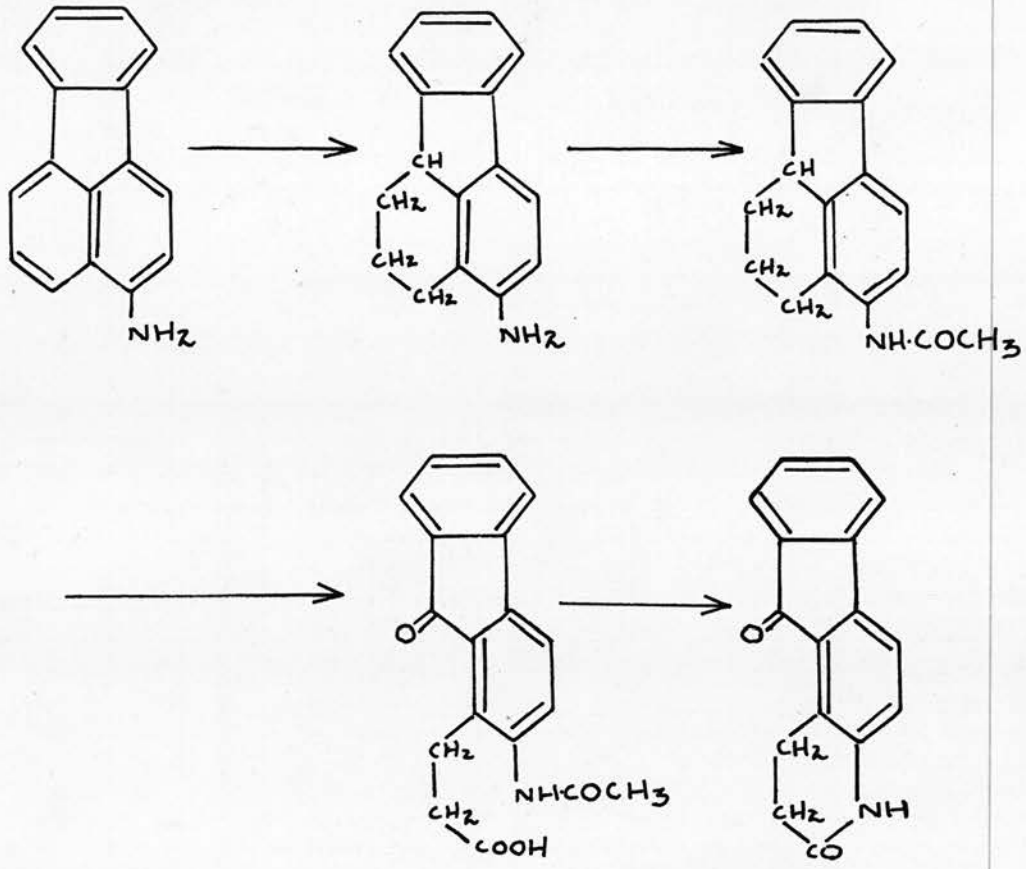
Five positions of mono-substitution (2,3,4,10, and 11) in the fluoranthene nucleus are available and the following evidence showed that the substituents were in the 4 position.

1. Bromofluoranthene was very easily reduced by sodium amalgam to 1:2:3:4 tetrahydrofluoranthene obtained synthetically by von Braun and Anton (loc. cit.,). Such an elimination of bromine showed that substitution occurred in the naphthalene half of the molecule.

2. 4-keto-1:2:3:4 - tetrahydrofluoranthene was reduced to the corresponding alcohol, and hydroxyfluoranthene was tetrahydrogenated. The secondary alcohols thus obtained were not quite identical, probably due to stereo-isomerism, but gave identical derivatives with phenyl isocyanate.

3. The unsubstituted ring of the naphthalene half of aminofluoranthene was tetrahydrogenated, similarly to α-naphthylamine and the ar-amino-5:6:7:8 - tetrahydrofluoranthene formed was acetylated and carefully oxidized to give a keto carboxylic acid having the same number of carbon atoms (cf Kruber, Ber., 1931, 64, 84). The product upon deacetylation was spontaneously converted by elimination of water into the corresponding lactam. This /

This was possible only if the amino group was in the 4-position.



von Braun and Manz in their next paper (Annalen, 1932, 496, 170) described investigations of the Friedel-Crafts reaction of fluoranthene. Oxalyl chloride and fluoranthene in the presence of aluminium chloride gave mainly a monocarboxylic acid along with a smaller amount of a dicarboxylic acid and a much smaller amount of a second monocarboxylic /

acid. Benzoyl chloride reacted with fluoranthene and aluminium chloride to give a monobenzoylfluoranthene with a smaller amount of a second monobenzoylfluoranthene. Similarly phthaloyl chloride gave two o-carboxybenzoylfluoranthenes, one of these in small amount only.

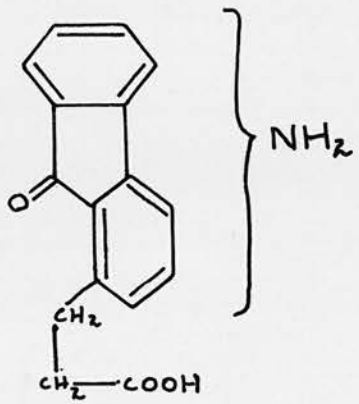
The monosubstituted products obtained in small quantity in the above reactions were shown to have identical orientations since the same aminofluoranthene was obtained from the oximes of benzoylfluoranthene and o-carboxylbenzoylfluoranthene by Beckmann transformation followed by hydrolysis and from the hydrazide of fluoranthene monocarboxylic acid by subjecting it to a Curtius degradation. Moreover, this aminofluoranthene was identical with 4-aminofluoranthene obtained in the previous series of investigations.

$$C_{16}H_9.CO.C_6H_5 \rightarrow C_{16}H_9C(=NOH).C_6H_5 \rightarrow C_{16}H_9.NH.CO.C_6H_5 \rightarrow C_{16}H_9NH_2$$

$$C_{16}H_9COOEt \rightarrow C_{16}HCO.NH.NH_2 \rightarrow C_{16}H_9CON_3 \rightarrow C_{16}H_9NCO \rightarrow C_{16}H_9NHCOOEt \rightarrow C_{16}H_9NH_2$$

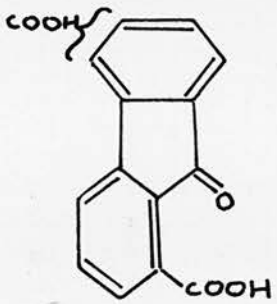
Similarly, the main monosubstituted products from the Friedel-Crafts reaction of fluoranthene were converted to the same amino: -fluoranthene, different from 4-aminofluoranthene. The possible positions of substitution for this main series of products were 2,3,10 and 11 and the actual position was shown to be 11 as follows:-

1. Reduction of the aminofluoranthene gave tetrahydro-aminfluoranthene and by careful oxidation this gave a stable aminofluorenone propionic acid



incapable of dehydration to a lactam thus confirming that the amino group was in position 2,3,10, or 11. The tetrahydro-aminofluoranthene was an ar- :tetrahydro compound and by consideration of the behaviour of α-naphthylamine, corresponding to the 2 or 3 position in fluoranthene, towards reduction it was improbable that the amino group was in position 2 or 3.

2. The fluoranthene monocarboxylic acid was oxidized to give a mixture of two fluorenone-dicarboxylic acids. The fact that two acids were formed showed that the carboxylic acid group was in the 10-or 11-position since isomers I and II were formedaccording as Ring I or II was split off. With the carboxylic acid group in the 2-or 3-position one would expect a single dicarboxylic acid. III or IV



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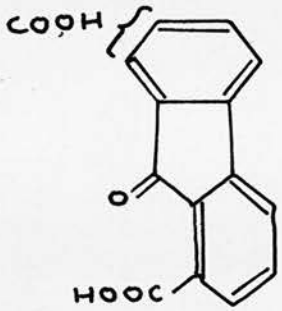

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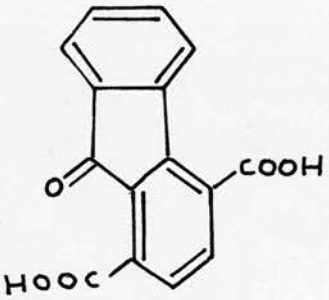

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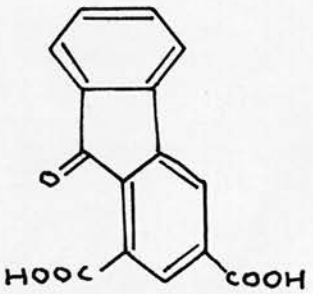

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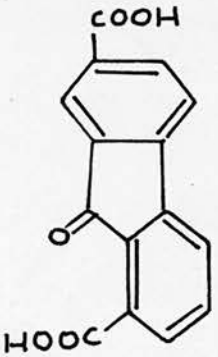


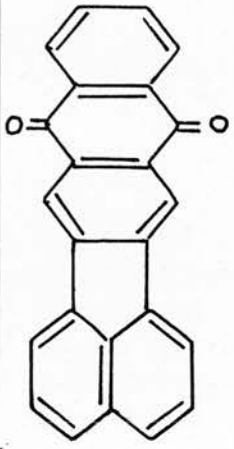
V

The mixture of acids was not separated but the methyl ester of one was said to show great similarity to the methyl ester of the acid V described by/

by Bamberger and Hooker (Annalen, 1885, 229, 102). Since, however, the two esters were not proved conclusively to be identical the original fluoranthene-carboxylic acid could not be identified with certainty as the 11- compound.

3. O-carboxybenzoylfluoranthene was ring closed to a mixture of two quinones. Now with the o-carboxy-benzoyl group in the 11- position two quinones, I and II would be formed, whereas with the group in the 10- position only one quinone II would be formed. (diagrams on following page). Upon oxidation, one of the quinones gave a quinone keto-carboxylic acid III which upon decarboxylation gave a keto quinone VI. The other quinone gave a mixture of two quinone keto-carboxylic acids, IV and V which was decarboxylated to VII and VIII although neither of the mixtures was separated. Zinc dust distillation of II gave the hydrocarbon IIa.

Recent work by Campbell et al. (see pp. 19, 23) showsthat the above cyclisation and oxidation experiments are not completely reliable and cannot be taken as conclusive evidence for the orientation of fluoranthene compounds since in some cases the structuresassigned by von Braun are definitely incorrect.



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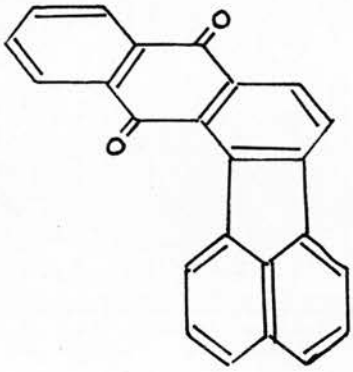
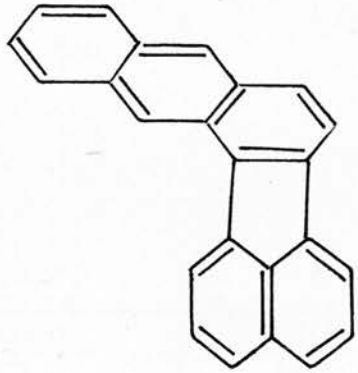
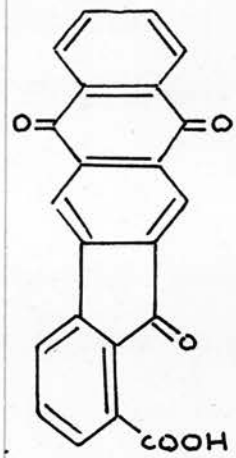


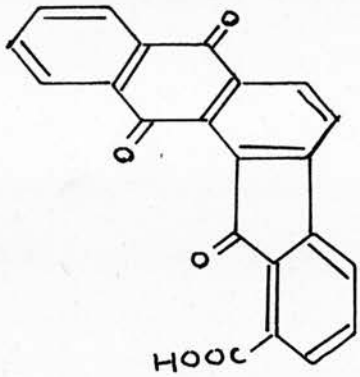
II



IIa



III



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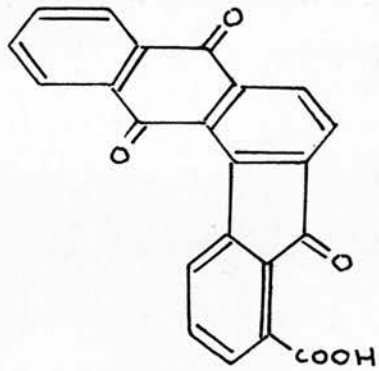

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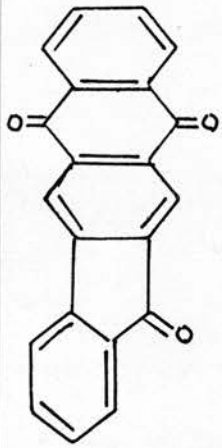

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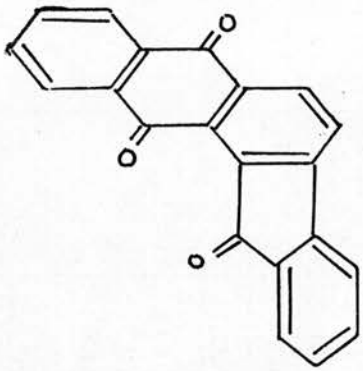
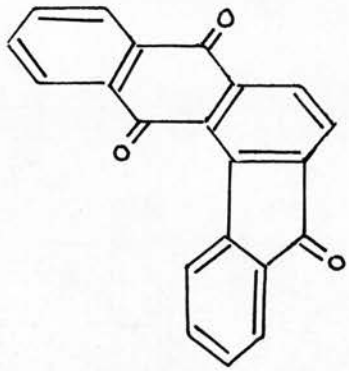


VII



VIII

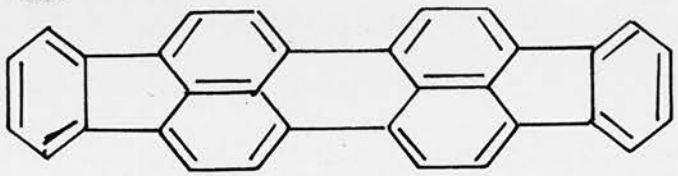
Having shown that the Friedel-Crafts reaction gave mainly 11-(12-) substitution with 4-substitution to a much smaller extent, whereas bromination, sulphonation and nitration gave mainly 4-substitution, the German workers then demonstrated that small amounts of 11-bromofluoranthene and 11-nitrofluoranthene could be detected in addition to the 4-compounds. The oxidation of 4-bromo, -nitro, and -carboxy-fluoranthenes to the 2-substituted fluorenone -1- carboxylic acids was described.

The above discoveries did not agree with experiments which showed that whereas 1:2:3:4-tetrahydrofluoranthene could be brominated or nitrated to give 4-bromo-5:6:7:8-tetrahydrofluoranthene or 4-nitro-5:6:7:8-tetrahydrofluoranthene as sole product, ?? phthaloyl chloride in the presence of aluminium chloride gave 4-O-carboxy-benzoyl-5:6:7:8-tetra-hydrofluoranthene as sole product instead of the ex-:pected 11- compound.

von Braun and Anton (Ber., 1934, 67, 1051) pointed out that α-phenylnaphthalene, which differs from fluoranthene only in the lack of a bond between carbon atoms 8 and 9, had been shown by previous workers /

workers to mononitrate and monobrominate- predominantly in the 4-position. They extended the work by showing that sulphonation gave exclusively that the 4-compound whereas benzoyl chloride in the presence of aluminum chloride also gave the 4-compound not the expected 11-benzoylfluoranthene.

In an attempt to prepare 4 amino-:fluoranthene by direct amination of fluoranthene with sodamide in boiling xylene, the compound shown below and named "periflanthene" was unexpectedly obtained by von Braun and Manz (Ber. 1937, 70 1603).



In connection with the study of this compound 4-phenyl and 4-methyl-fluoranthene were synthesised from 4-keto-1:2:3:4 - tetrahydro-fluoranthene by Grignard reaction followed by dehydrogenation.

A patent (G.P. 575, 953; Ch.Abs. 1933 27, 4819) described the preparation of a dihydroxy-:fluoranthene by sulphonating fluoranthene and fusing/

fusing the resulting disulphonic acid with alkali.

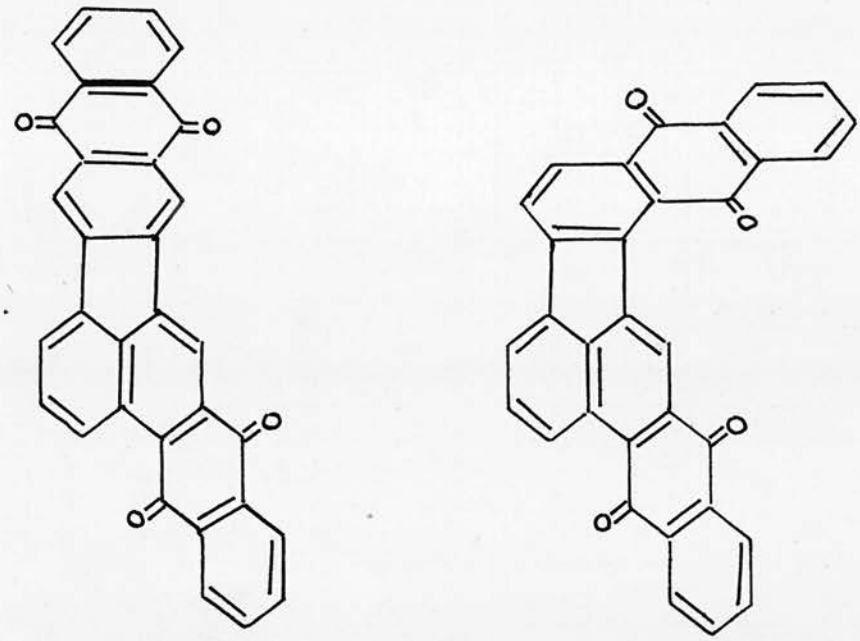
Bergdolt and Ballanf (U.S. 1,990,018; Ch.Abs., 1935, 29, 1998) patented a similar process and also described the production of 3-,4-, and 11-hydroxyfluoranthenes, and 11-hydroxyfluoranthene o-carboxylic acid.

The production of 4- and 11- hydroxy-:fluoranthene-monosulphonic acids and 4-hydroxy-:fluoranthene - disulphonic acid by the action of concentrated sulphuric acid on hydroxyfluoranthenes has been described (B.P. 469, 927; Brit. Abstracts, (B), 1937, 1176) and fluoranthene monosulphonic acid may be prepared from 4-aminofluoranthene by reacting with the equivalent of chlorosulphonic acid (G.P. 711, 159 ; Ch. Abs., 1943, 37, 4078).

Another patent (B.P. 533, 962; Ch. Abs., 19 1942, 36, 1190) described the conversion of dibromofluoranthene (now known to be the 4:11-compound) to dicyandfluoranthene and hence the dicarboxylic acid. Dibromofluoranthene was also converted to diaminofluoranthene which gave dicyano-:fluoranthene by tetrazotisation followed by the Sandmeyer reaction. Tricyanofluoranthene and the tricarboxylic acid were also described.

von Braun (B.P. 468, 648; Chem. Zent. ., 1938I, 738) claimed that by heating fluoranthene

with excess phthaloyl chloride a condensation product was formed with two molecules of phthalic anhydride and suggested that the product was not uniform but a mixture of I and II below.



I II

Tobler, Holbro, Sutter and Kern (Helv. Chim. Acta, 1941, 24 100E) studied the bromofluoranthenes. They prepared 4-bromofluoranthene by dehydrogenating 4-bromo-5:6:7:8- tetrahydrofluoranthene. The preparation of dibromofluoranthene was described and it was suggested, but not proved, that the bromine atoms were in positions 4- and 11-.

A synthesis of this compound from 2:7-dibromofluorenone was unsuccessful, but 4:11-dibromo-5:6-benzfluoranthene was synthesised from 2:7-dibromofluorene. The tribromofluoranthene described by /

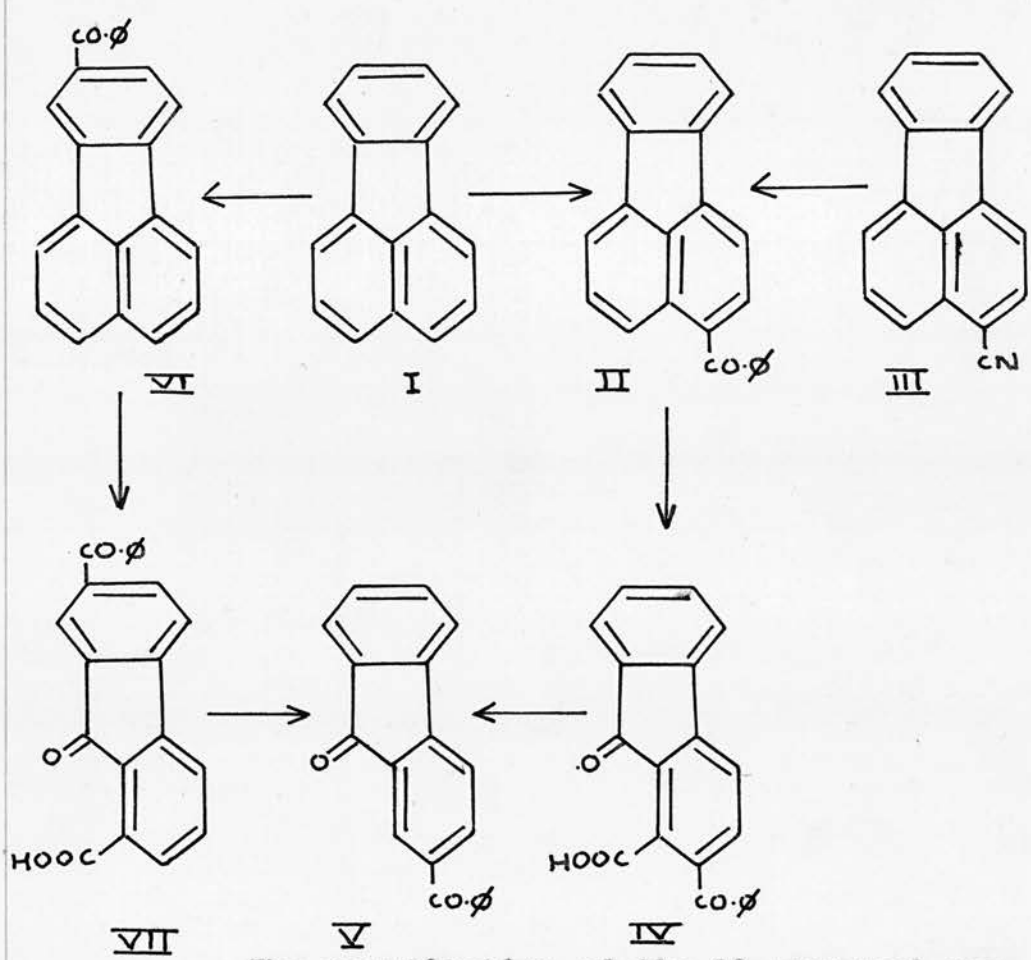
by Goldschmidt (loc. cit.) could not be obtained but a different tribromofluoranthene and also a tetrabromofluoranthene were prepared.

Buu-Hoï and Cagniant (Rec. Trav. Chim., 1943 62, 719) reported the action of acetyl chloride on fluoranthene in the presence of aluminium chloride and claimed that 11-acetyl-:fluoranthene was formed. No 4-acetylfluoranthene or diacetylfluoranthene was obtained. The compound was orientated by converting its oxime to 11-acetamidofluoranthene by the Beckmann transformation.

The same workers (Ber., 1944, 77B, 121) stated that in the action of tert-butyl chloride on fluoranthene in the presence of aluminium chloride a compound claimed to be 4:11-di-tert-butylfluoranthene was obtained. The analysis and molecular weight were determined, but no evidence for the orientation was given.

The Friedel-Crafts reaction of fluoranthene was reinvestigated by Campbell and Easton (J., 1949 340). The reaction of fluoranthene with benzoyl chloride in the presence of aluminium chloride gave 4- and 11- benzoylfluoranthene. The constitution of the 4- compound was shown by its preparation from 4-cyano fluoranthene III. Oxidation of 4-benzoyl-:fluoranthene /

:fluoranthene II gave 1-carboxy-2-benzoyl-fluorenone IV, which on decarboxylation gave 2-benzoylfluorenone V.



The constitution of the 11-compound was proved since on oxidation it gave 7-benzoylfluorenone-1-carboxylic acid identified by the fact that it gave 2-benzoyl-:fluorenone on decarboxylation.

Oxalyl chloride with fluoranthene in the Friedel-Crafts reaction gave fluoranthene - 11-carboxylic acid and a dicarboxylic acid, decarboxylation experiments with these acids being described.

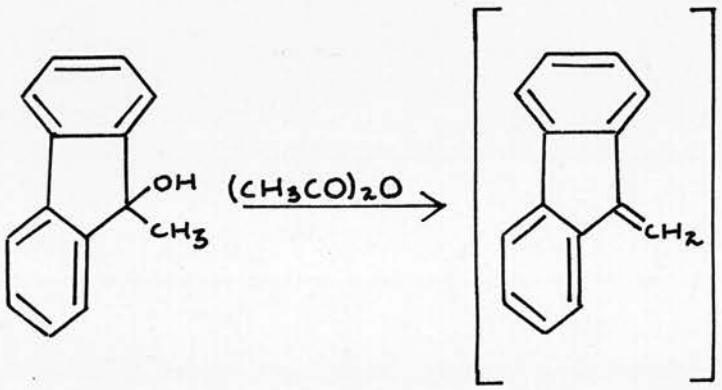
Phthaloylation/

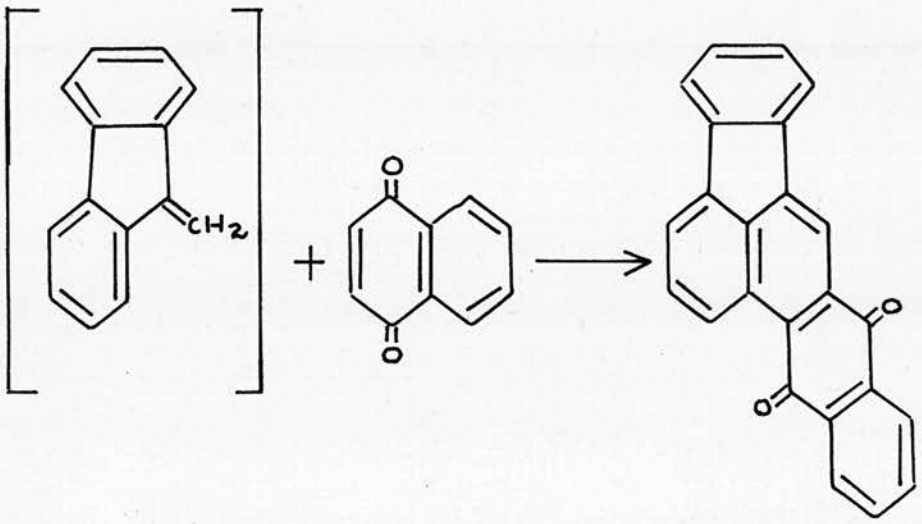
Phthaloylation gave 4- and 11-o-carboxybenzoylfluoranthene, their structures being confirmed by decarboxylation to the corresponding benzoylfluoranthenes.

Acetylation of fluoranthene gave 4-acetylfluoranthene, identical with a sample prepared from 4-cyanofluoranthene; an isomer which was probably 11-acetylfluoranthene; and a diacetyfluoranthene. Thus the 11- acetylfluoranthene described by Buu-Hoi and Cagniant (loc. cit.) was very impure.

Benzoyl chloride reacted with 1:2:3:4-tetrahydrofluoranthene in the presence of aluminium chloride to give mainly 5-benzoyl-1:2:3:4-tetrahydrofluoranthene with a small amount of an isomer and a dibenzoyl-tetrahydrofluoranthene.

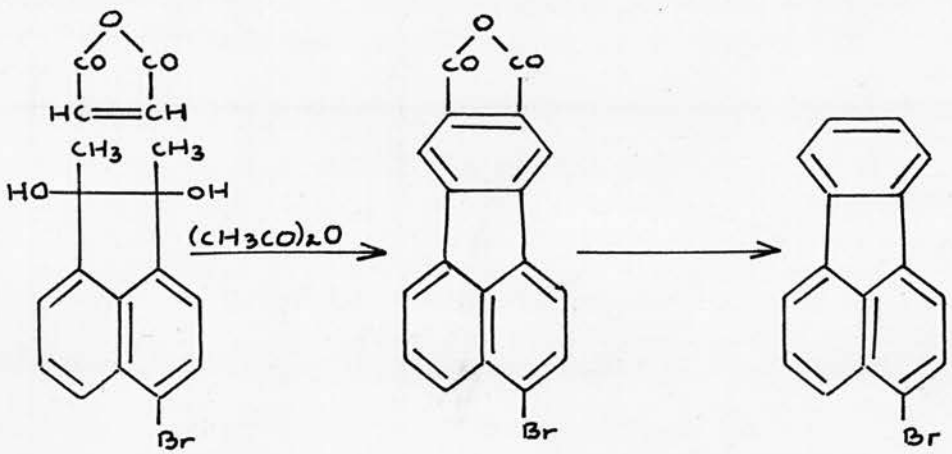
Campbell and Wang (J., 1949, 1513; Nature 1948, 162, 857) described the synthesis of several fluoranthene derivatives using the Diels-Alder reaction. In connection with substitution studies their synthesis of naphtho (2':3':-3:4) fluoranthene -1':4'- quinone by condensing 9-hydroxy - 9-methylfluoranthene with 1:4- naphthoquinone in the presence of acetic anhydride is important:-



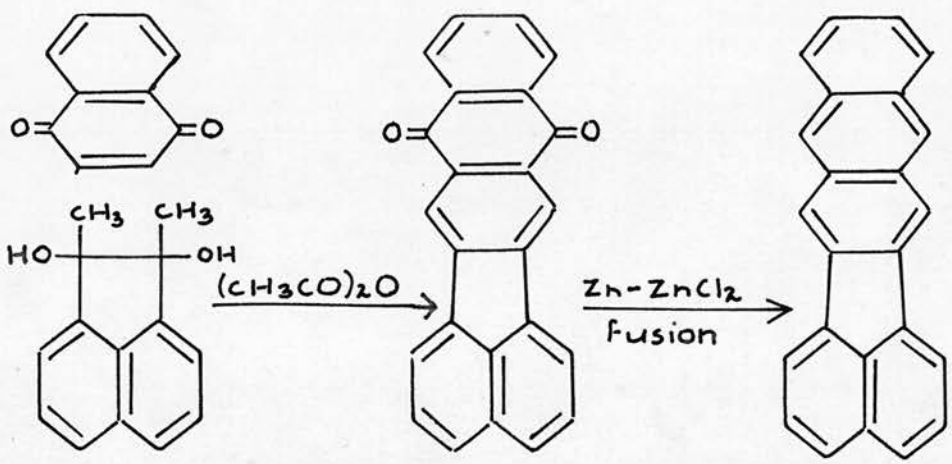


This quinone was claimed by von Braun and Manz (Annalen, 1932, 496, 170) to be formed by the cyclisation of 4-O-carboxybenzoylfluoranthene, but the quinone described by them was different from the one synthesised unambiguously as above.

Some of the work of Campbell and Gow J., 1949, 1555; Nature, 1948, 162 857) also deals with compounds described by von Braun and Manz. 4-bromofluoranthene was synthesised as shown below thus confirming some of von Braun's orientation studies,

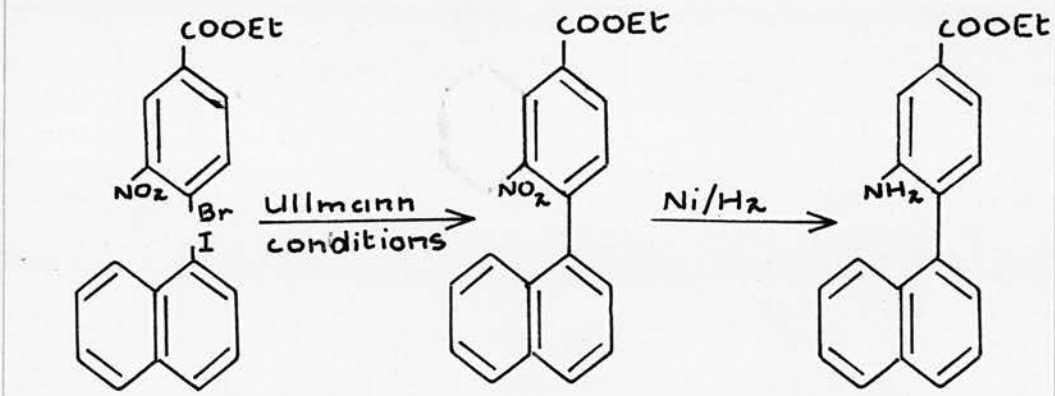


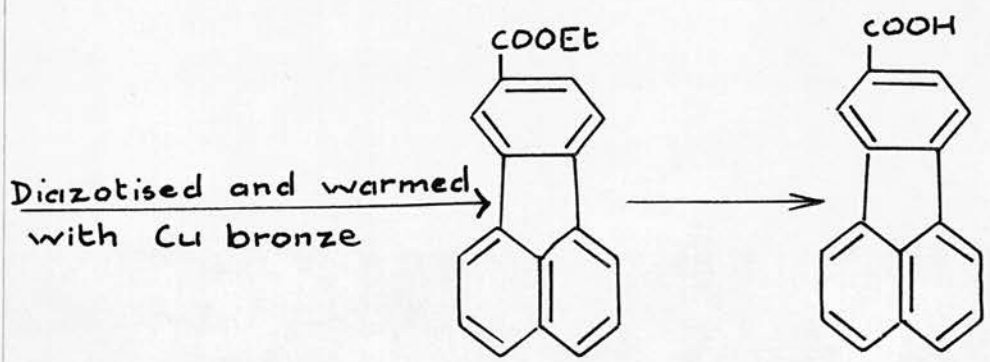
Naphtho (11':12'-2:3) fluoranthene -1:4-quinone and the corresponding hydrocarbon were synthesised as follows



The properties of this quinone and hydrocarbon showed that the structures assigned by von Braun to the two quinones obtained by cyclising 11-O-carboxybenzoylfluoranthene (see pp. 9,10.) should be reversed.

The orientation of the substituent group in fluoranthene -11- carboxylic acid was confirmed by Tucker and Whalley (J., 1949, 3213) who synthesised this compound as follows.

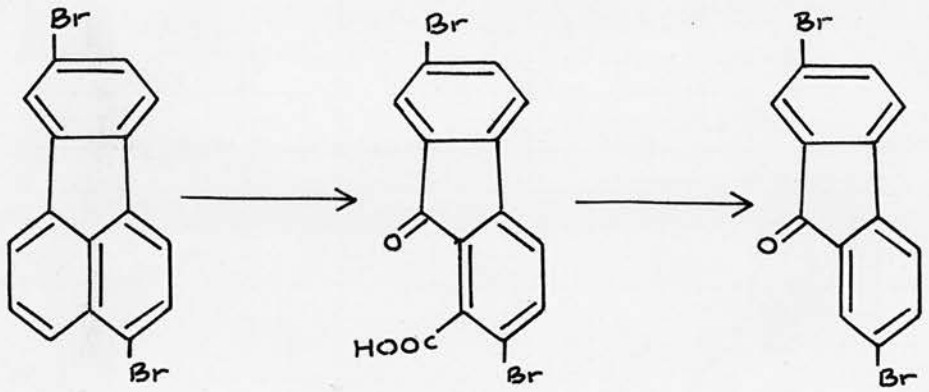




10- and 11- methylfluoranthene were similarly synthesised/

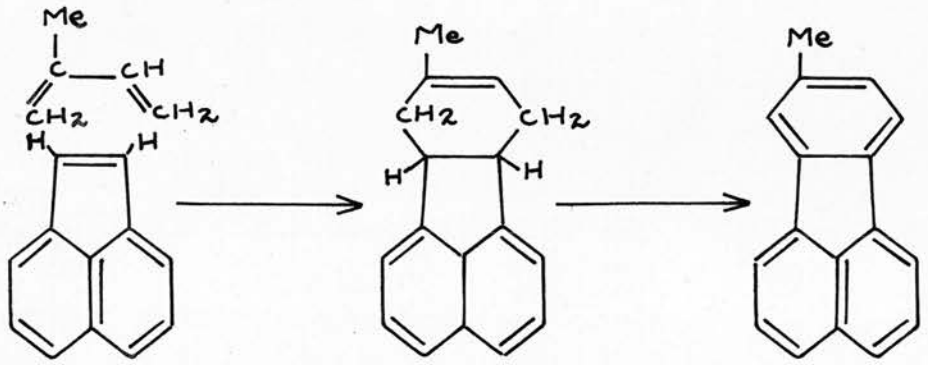
synthesised. Fluoranthene -11- carboxylic acid was converted to 11-methyfluoranthene.

The bromine atoms in dibromofluoranthene were shown to be in the 4:11-positions by Campbell et al. (J., 1950, 2784; Nature 1950, 165, 176) who oxidised dibromofluoranthene to 2:7- dibromo-:fluorenone -1- carboxylic acid, whose structure was proved by decarboxylation to 2:7- dibromo-:fluorenone.

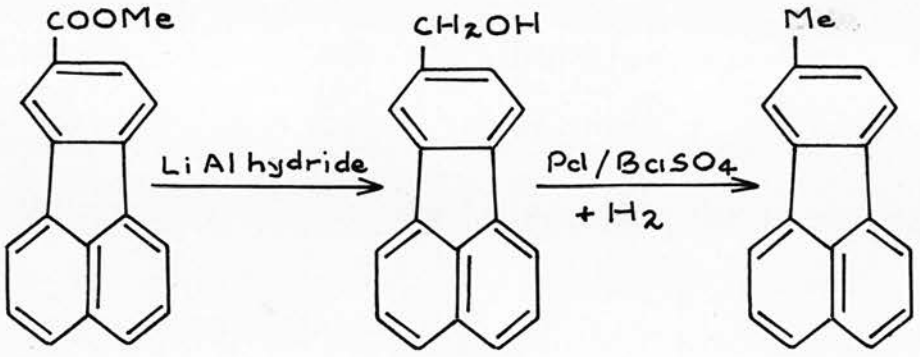


Bergmann(Nature, 1948, 161, 889) synthesised several fluoranthene derivatives other than 4- and 11- compounds by reacting acenaphthylene with butadiene derivatives. Kloetzel and Mertel (J. Amer.Chem.Soc., 1950, 72, 4786) used the same method to synthesise 11- methylfluoranthene by reacting/

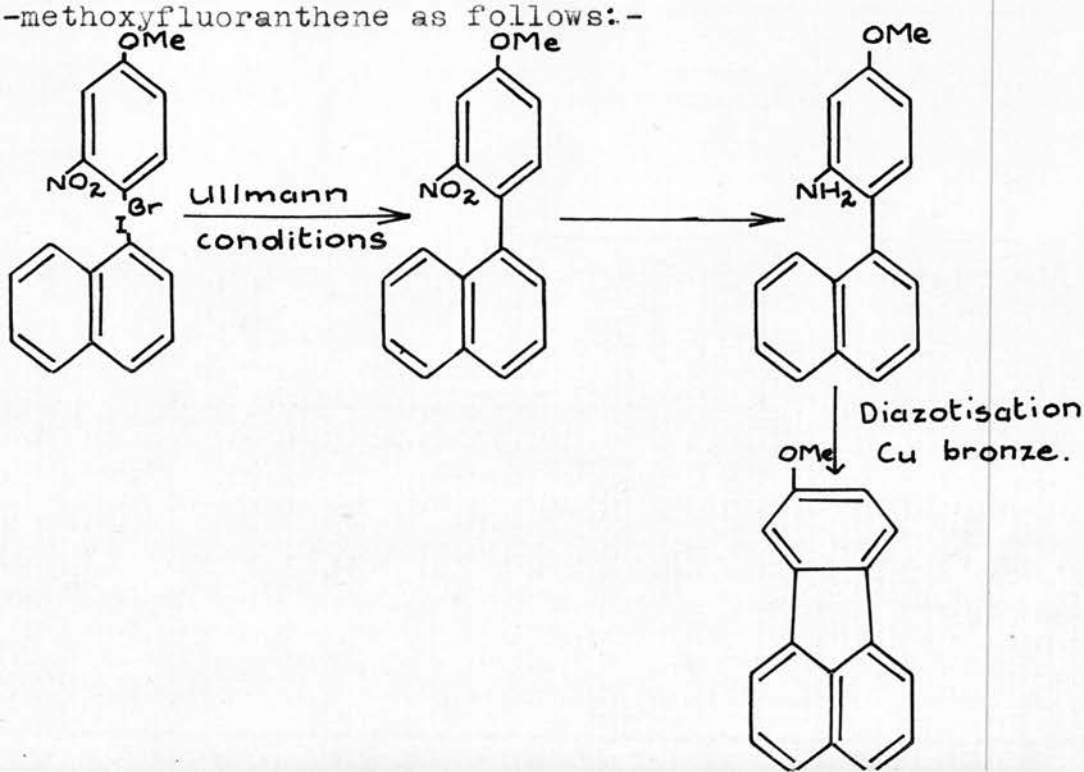
reacting acenaphthylene with isoprene and dehydrogenating the product.



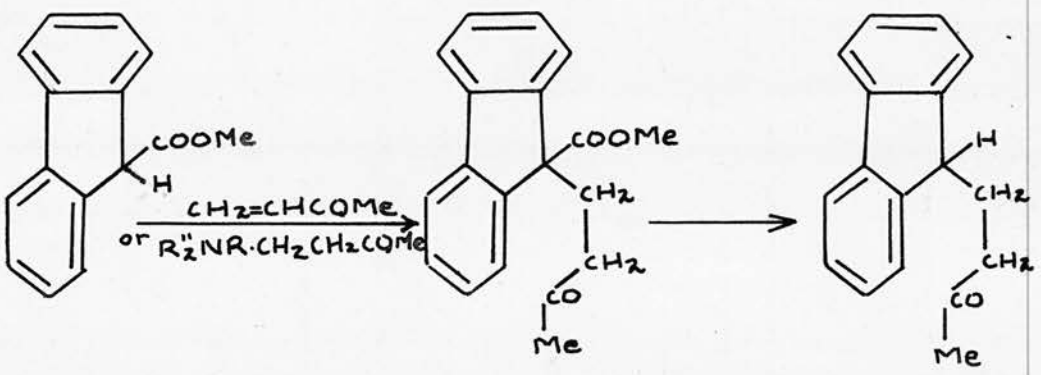
11-Methylfluoranthene was also prepared from methyl fluoranthene-11-carboxylate as follows:-

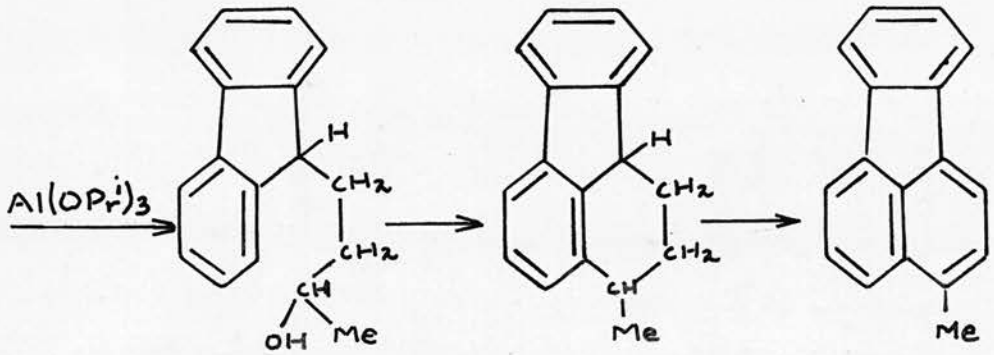


Hawkins and Tucker(J.,1950,3286) synthesised 11-methoxyfluoranthene as follows:-



Stubbs and Tucker (J., 1950, 3288) synthesised 4-methylfluoranthene by the reaction between methyl fluorene -9- carboxylate and methyl vinyl ketone, $CH_2{=}CHCOCH_3$ (or the quaternary salt of the corresponding Mannich base $R_2N{\cdot}CH_2CH_2COMe$), and subsequent cyclisation.

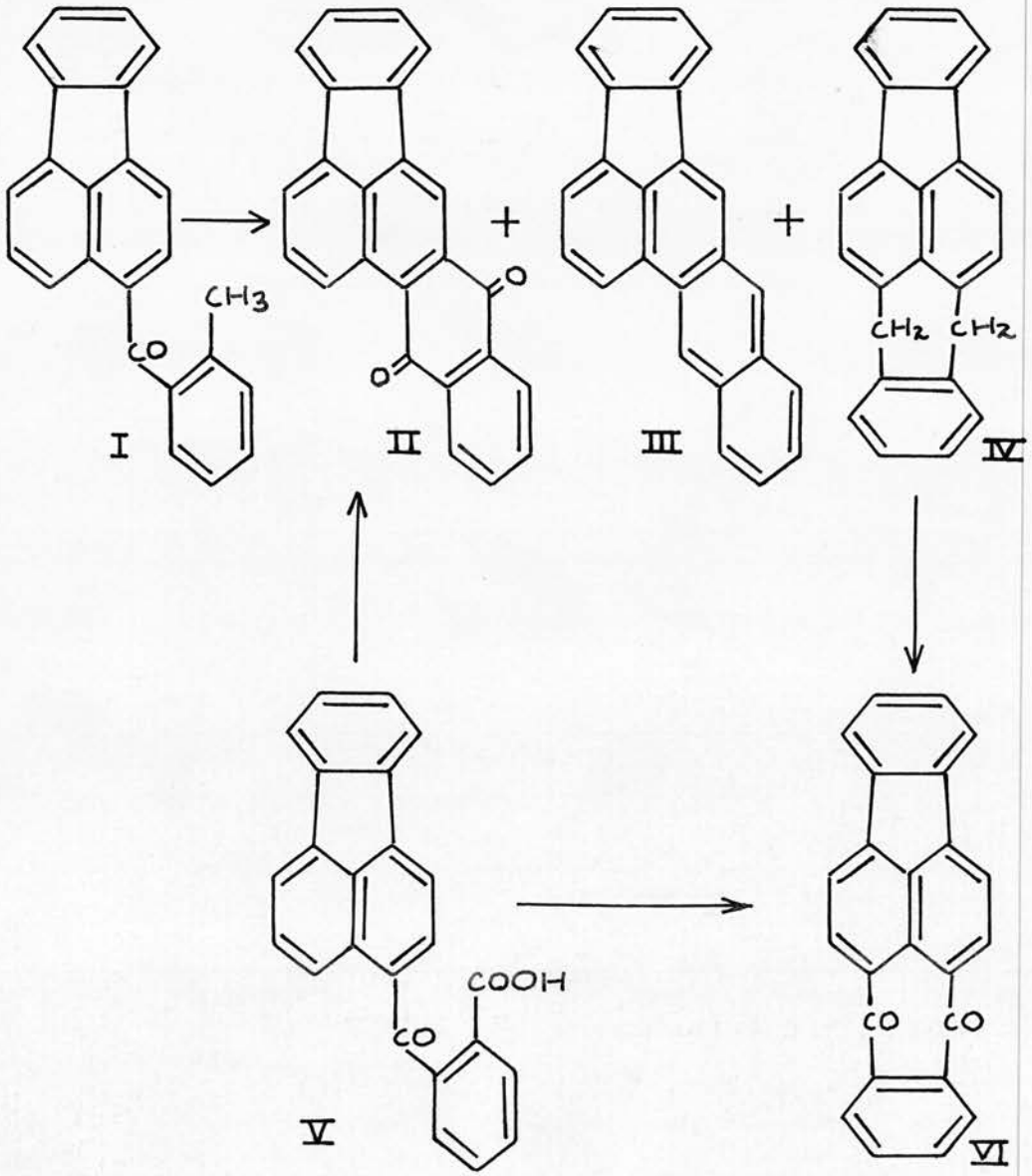




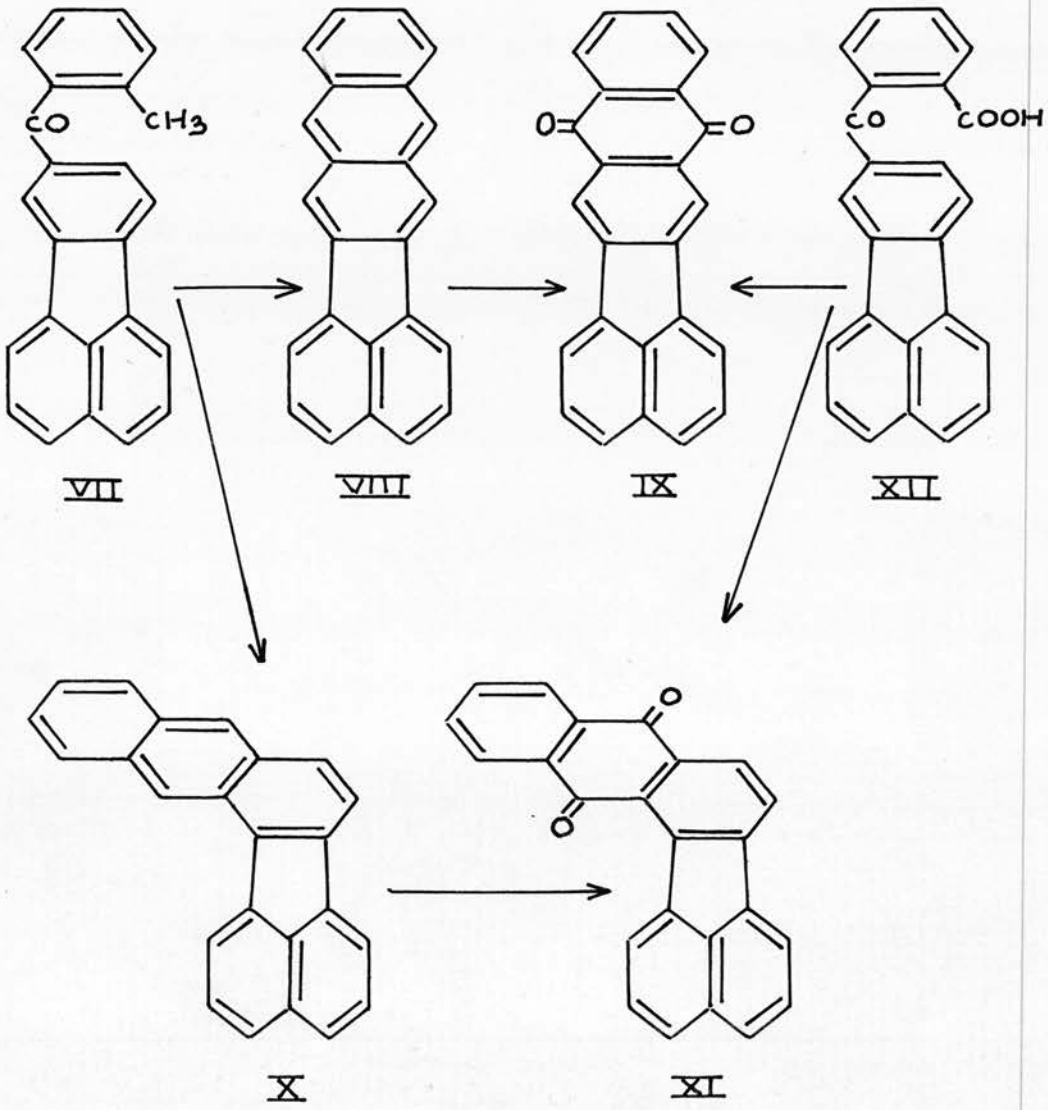
4-Phenylfluoranthene was similarly synthesised.

Some cyclisation experiments were described by Campbell, Marks, and Reid (J., 1950, 3466). 4-o-Toluylfluoranthene I, subjected to the /

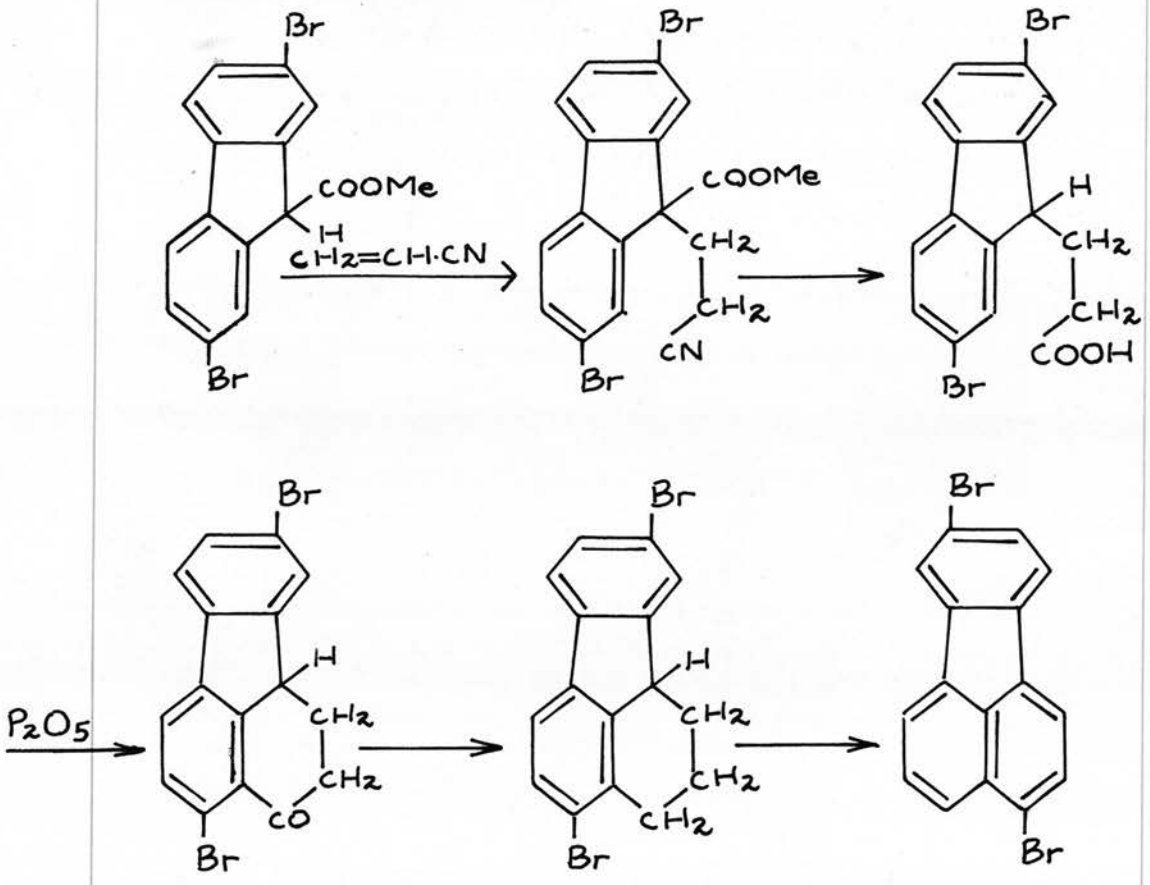
the Elbs reaction gave a mixture of naphtho (2':3'-3:4) fluoranthene -1':4' quinone II; naphtho (2':3'-3:4) fluoranthene III; and a hydrocarbon which was presumably 4:5-0- xylylenefluoranthene IV since its oxidation gave 4:5- phthaloylfluoranthene VI. Ring closure of 4-0- carboxybenzoylfluoranthene gave II and VI, neither of which corresponded to the quinone isolated by von Braun in his ring closure of 4-0- carboxybenzoylfluoranthene and claimed to have the structure II.



11-O- Toluylfluoranthene VII, in the Elbs reaction, gave naphtho (2':3'-11:12) fluoranthene VIII and naphtho (2':3'-10:11) fluoranthene X, both of which could be oxidized to the quinones IX and XI. Ring closure of 11-O-carboxybenzoylfluoranthene XII gave IX and XI, but no trace was found of the substance claimed by von Braun to be XI.



Holbro and Tagmann (Helv. Chim. Acta, 1950, 33, 2178) confirmed that dibromofluoranthene has the constitution 4:11-dibromofluoranthene by synthesising it from methyl 2:7- dibromofluorene-9- carboxylate.



DISCUSSION OF EXPERIMENTAL RESULTS.

(A) THE ACETYLATION OF FLUORANTHENE.

A survey of published work on the Friedel-Crafts reaction of fluoranthene shows that disubstituted products may be formed in addition to 4- and 11- monosubstituted compounds. Thus oxalyl chloride and fluoranthene in the presence of aluminium chloride give a fluoranthene dicarboxylic acid (von Braun and Manz, Annalen, 1932, 496, 170; Campbell and Easton, J., 1949, 340); acetyl chloride gives diacetylfluoranthene (Campbell and Easton loc. cit.), and tert- butyl chloride gives di-tert- butylfluoranthene (Buu-Hoi and Cagniant, (Ber., 1944, 77B,121). These disubstituted products have never been orientated.

It has been proved that bromination of fluoranthene gives 4:11- dibromofluoranthene (Campbell et al., Nature, 1950, 165, 76; J., 1950, 2784; ibid, 1951, 1137; Holbro and Tagmann, Helv. Chim. Acta, 1950, 33, 2178), and it has been suggested (Tobler et al., Helv. Chim. Acta, 1941, 24, 100E) that sulphonation gives fluoranthene -4:11- disulphonic acid.

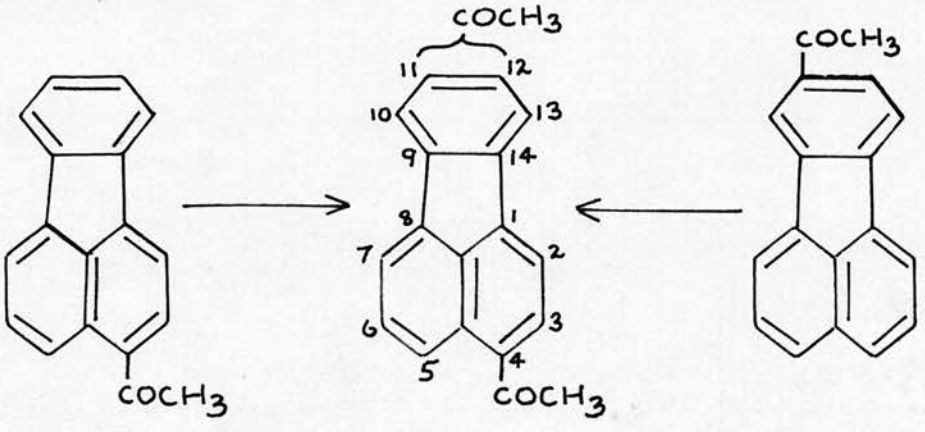
The /

The orientation of the disubstituted products of the Friedel-Crafts reaction cannot be inferred from this orientation of dibromo-:fluoranthene, however, and an investigation of the products of the action of acetyl bromide on fluoranthene in the presence of aluminium chloride was accordingly undertaken. Details of this investigation are given below.

<u>The acetylation of fluoranthene and acetyl-:fluoranthenes</u>.

Fluoranthene, and acetyl bromide reacted in the presence of aluminium chloride to give a mixture of 4-acetyfluoranthene, 11-acetyl-:fluoranthene, diacetylfluoranthene, and unchanged fluoranthene. Increasing the time of the reaction gave a higher yield of diacetylfluoranthene and hardly any unchanged fluoranthene

Both 4-acetylfluoranthene and 11-(12-) acetyfluoranthene upon further acetylation yielded the same diacetylfluoranthene thus showing that the latter was either 4:11- or 4:12- diacetyl-:fluoranthene



Diacetylfluoranthene, by Brady's method, gave only a mono -2:4- dinitrophenylhydrazone whereas Campbell and Easton report that both 4- and 11- acetylfluoranthenes form 2:4- dinitrophenyl- hydrazones by Allen's method. These workers also found that whilst 11- benzoylfluoranthene readily gave a 2:4- dinitrophenylhydrazone by Brady's method 4-Benzoylfluoranthene formed a derivative only after boiling under reflux for several hours. It appears that there is some interaction between the substituent groups in diacetylfluoranthene which permits only one carbonyl group (probably at the 11- position) to react with 2:4- dinitrophenylhydrazine.

Oxidation of acetylfluoranthenes.

Of the two possibilities demonstrated above, the substituent groups in diacetylfluoranthene were shown to be in the 4:12- position by oxidation to a fluoranthene-dicarboxylic acid which was identical with the acid obtained by the action of oxalyl chloride on fluoranthene in the presence of aluminium chloride (Campbell and Easton, loc. cit.), but different from fluoranthene-4:11- dicarboxylic acid prepared from 4:11- dibromo- :fluoranthene via the nitrile by Campbell and Wilshire/

Wilshire (J., 1951, 1404). Since the free acids have high melting points, the methyl esters were used in comparisons. All these results show that Friedel-Crafts disubstituted products are 4:12- diacetylfluoranthene and fluoranthene - 4:12- dicarboxylic acid.

The compound claimed by Buu-Hoï and Cagniant to be 11- acetylfluoranthene, and orientated by them by conversion to 11-acetamido- :fluoranthene, was shown by Campbell and Easton to be a mixture and the latter workers obtained a mono-acetylfluoranthene thought to be 11- acetyl- :fluoranthene, but which was not orientated. This compound has now been orientated by its oxidation to fluoranthene -11- carboxylic acid, identified by comparison of its methyl ester with Campbell and Easton's methyl fluoranthene -11- carboxylate acid, of its ethyl ester with ethyl fluoranthene -11- carboxylate synthesised by Tucker and Whalley (J., 1949, 3213).

Oxidations were best performed with sodium hypochlorite rather than alkaline permanganate. The latter, due to the quantities required, was thought to give some rupture of the fluoranthene/

fluoranthene nucleus and also gave lower yields and less pure products than hypochlorite oxidation.

Decarboxylation of fluoranthene -4:12- dicarboxylic acid.

The decarboxylation of fluoranthene -4:12- dicarboxylic acid has been described by Campbell and Easton (loc. cit.) but the experiment was not entirely satisfactory since it was performed on a very small scale. It was claimed that fluoranthene -4- carboxylic acid. was readily decarboxylated by copper bronze in hot quinoline whereas the 11-(12-) acid was unaffected under these conditions. Fluoranthene -4:12- dicarboxylic acid was thought to decarboxylate to fluoranthene -11- carboxylic acid, the presence of a small amount of fluoranthene being due to fluoranthene -4- carboxylic acid impurity in the dicarboxylic acid.

In the present investigations, it was found that fluoranthene -4:12- dicarboxylic acid gave a 32% yield of fluoranthene, showing that the latter was not due to the decarboxylation of an impurity. In another experiment, under the same conditions, no fluoranthene was observed but/

but fluoranthene -11- carboxylic acid was indicated thus giving further evidence for the position of the substituents in the fluoranthene dicarboxylic acid. Finally, milder conditions were used for decarboxylation and an attempt was made to isolate the acidic products as the methyl esters, but unfortunately the main product could not be completely purified. The product was shown to contain chlorine and since the fluoranthene -4:12- carboxylic acid used was of a batch different from that previously used it had presumably chlorinated during its preparation by hypochlorite onidation

Repetition of Campbell and Easton's work confirmed that fluoranthene -11- carboxylic acid is not decarboxylated when subjected to conditions that cause fluoranthene -4:12- dicarboxylic acid to decarboxylate to fluoranthene. It thus appears as if the 4-carboxy group in the 4:12- dicarboxylic acid has some effect upon the 11- carboxy group

<u>The Schmidt reaction on acetylfluoranthenes.</u>

von Braun and Manz in their orientation of Friedel-Crafts products converted the ketoximes to the corresponding acetamidofluoranthenes by the Beckmann transformation. The acetylfluoranthenes have/

have now been converted to acetamidofluoranthenes by the simpler Schmidt reaction.

The Schmidt reaction (cf. H. Wolfe, in Adams' "Organic Reactions" III) is the reaction between hydrazoic acid and carbonyl compounds in the presence of a suitable catalyst. Thus amines may be prepared from acids,

$$RCOOH + HN_3 \xrightarrow{H_2SO_4} RNH_2 + CO_2 + N_2$$

aldehydes yield nitriles and formyl derivatives of amines, and ketones yield amides.

$$RCHO + HN_3 \xrightarrow{H_2SO_4} RCN \text{ and } RNHCHO$$

$$RCOR + HN_3 \xrightarrow{H_2SO_4} RCONHR + N_2$$

Dice and Smith (J. Org. Chem., 1949, 14, 179) used the reaction to convert acetyl - and benzoyl-phenanthrenes into acetamido - and benzamido phenanthrenes. For unsymmetrical ketones it is theoretically possible to get two isomeric amides by either the Beckmann or the Schmidt reaction.

$$R'COR \longrightarrow R'NHCOR + RNHCOR'$$

In the Beckmann transformation of aryl methyl ketones the N- arylacetamide is the predominant product and the work of Dice and Smith suggested that the same generalisation could be applied to the Schmidt reaction.

In view of the expected similarity of acetyfluoranthenes/

acetylfluoranthenes and acetylphenanthrenes towards hydrazoic acid the same reaction conditions were used in the present investigations as were used for the conversion of acetylphenanthrenes to acetamido-:phenanthrenes. The acetylfluoranthene was dissolved in trichloro-acetic acid, which also acted as a catalyst, and treated with excess sodium azide for 8 hours at 60°.

In this way 11- acetylfluoranthene was converted to 11- acetamidofluoranthene, m.p. 199-201°, previously prepared from other ketoximes, but not analysed, by von Braun and Manz 'Annalen, 1932, 496, 170) whose product was obviously not pure since its melting point was 190°. This reaction with 11-acetylfluoranthene confirmed the orientation of the latter, previously shown by its oxidation to fluoranthene -11- carboxylic acid.

4-acetylfluoranthene was converted into 4-acetamidofluoranthene, the hydrolysis of which gave 4- aminofluoranthene.

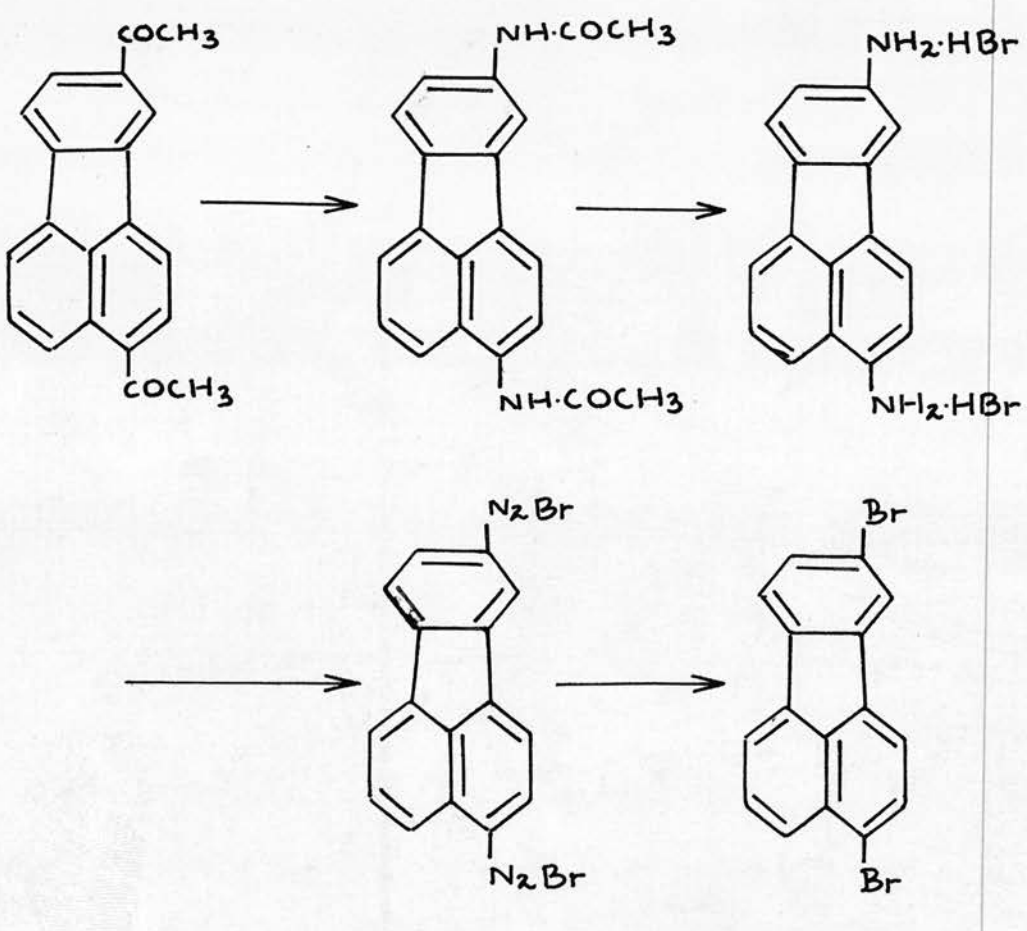
The Schmidt reaction on 4:12- diacetyl-:fluoranthene yielded 4:12- diacetamidofluoranthene which was readily hydrolysed by concentrated hydrochloric acid or hydrobromic acid to 4:12-diaminofluoranthene dihydrochloride or the corresponding hydrobromide.

The /

The free diamine was liberated from its salts by aqueous ammonia or sodium hydroxide but could not be obtained pure.

Its picrate was prepared and analysed, however.

Further proof that the substituents in diacetylfluoranthene are in the 4:12- positions was obtained by tetrazotising either diaminofluoranthene dihydrochloride or dihydrobromide and performing a Sandmeyer reaction with cuprous bromide and hydrobromic acid on the tetrazonium salt to give a dibromofluoranthene which was shownto be different from 4:11- dibromofluoranthene.



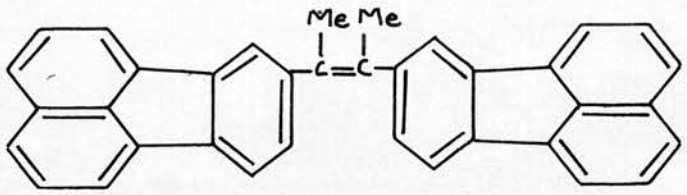
Since the acetylation of 4- and 11-acetylfluoranthenes has already shown that diacetyl-:fluoranthene is either the 4:12- or 4:11- compound, this dibromofluoranthene must be 4:12- dibromofluoran-:thene and the diacetylfluoranthene is the 4:12- compound.

Reduction of Acetylfluoranthenes.

Unsuccessful attempts were made to reduce the acetylfluoranthenes to ethylfluoranthenes which would have been useful reference compounds in the study of fluoranthene derivatives.

Reduction of 4:12- diacetylfluoranthene by the modified Wolff-Kishner method (Huang - Minlon, J. Amer. Chem. Soc., 1946, 2867) gave a high melting impure compound which contained nitrogen and was probably an azine. Clemmensen reduction gave only unchanged material.

Clemmensen reduction of 11—acetylfluoranthene gave a product whose high melting point suggests it is not the ethyl derivative but the dimeric 2:3-di-(11-fluoranthyl) but -2-ene shown below



Clemmensen reduction of 4- acetylfluoranthene gave impure high melting material which was probably dimeric and contained substances of the type 2:3-di-(4-fluoranthyl) but -2-ene.

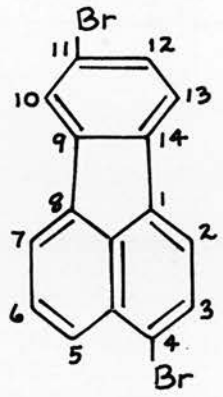
The /

The picrates of these reduction products of the mono-acetylfluoranthenes could not be obtained pure but their analyses suggest that they consist of two molecules of picric acid combined with one molecule of dimer.

Formation of dimeric materials in the Clemmensen reduction of ketones is not unusual. (cf. Adams' "Organic Reactions" I. p. 155). Thus Steinkopf and Wolfram (Annalen, 1923, 430, 113) showed that benzophenone when reduced with amalgamated zinc and aqueous hydrochloric acid gave benzpinacol and traces of diphenyl-methane. When alcoholic hydrochloric acid was used, tetraphenyl ethylene, α and β benzpinacolin, and diphenyl-methane were obtained. Under the first conditions, acetophenone gave ethyl-:benzene, acetophenonepinacolin, styrene and its polymerisation products whilst alcoholic conditions gave styrene and its polymerides, acetophenonepinacol, and α-chloro-ethylbenzene. Similarly, Bradlow and Vander Werf (J. Amer.Chem.Soc. 1947, 69, 1254) gave many examples in which Clemmensen reduction of aromatic ketones leads to resinous products.

(B.) THE ACETYLATION OF 4:11- DIBROMOFLUORANTHENE

The work outlined above on the Friedel-Crafts reaction of fluoranthene was next extended by an investigation of the action of the same reagents on 4:11 dibromofluoranthene.



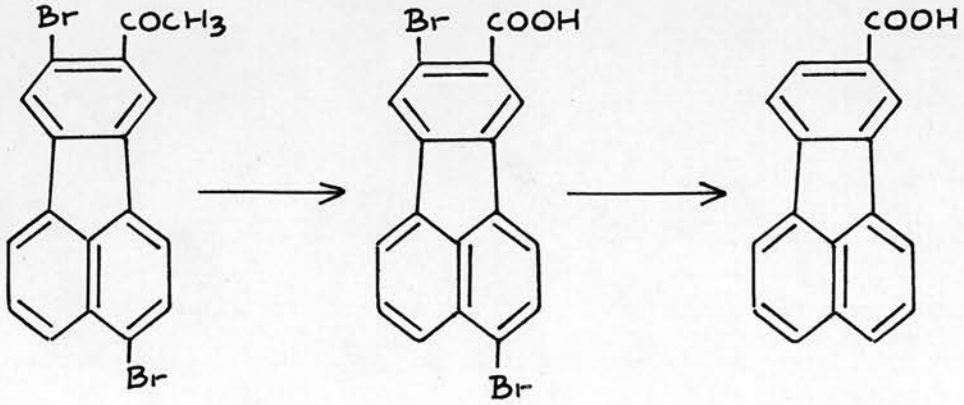
All known products from the substitution of fluoranthene have their substituents in the 4-(5-) 11-(12-), 4:11, or 4:12- positions and it was thus thought that 4:11- dibromofluoranthene would be attacked in the 5- or the 12- position to give either 4:11- dibromo-5- acetylfluoranthene or 4:11- dibromo -12- acetylfluoranthene, or a mixture of both.

Actually, only one product was obtained, in a yield of 56% of the theoretical, and the subsequent reactions given below showed this compound to be 4:11- dibromo -12- acetylfluoranthene.

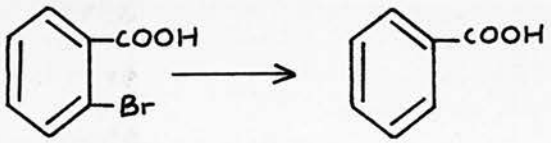
The/

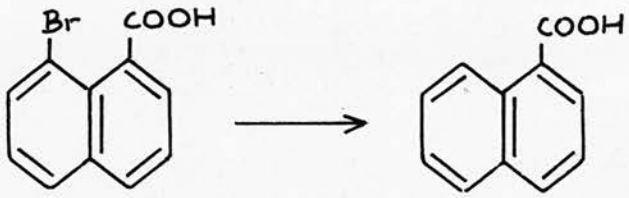
The 4:11- dibromo - acetylfluoranthene was readily oxidized with sodium hypobromite to give 4:11- dibromofluoranthene-carboxylic acid whose methyl ester was also prepared. The carboxylic acid was not very soluble in the usual organic solvents and its sodium salt was only very slightly soluble in water. Oxidation with sodium hypochlorite gave mainly unchanged material. Oxidation with alkaline permanganate gave mainly unchanged material and an acid thought to be produced by cleavage of the fluoranthene skeleton, but this acid was not investigated.

Both bromine atoms in the 4:11- dibromo-:fluoranthene-carboxylic acid were readily removed by reduction with Raney nickel-aluminium alloy in alcoholic caustic potash. The monocarboxylic acid produced was shown to be fluoranthene -11- carboxylic acid by comparison of both the free acid and its methyl ester with authentic samples. Thus the original 4:11- dibromo-acetylfluoranthene must have been 4:11- dibromo -12- acetylfluoranthene

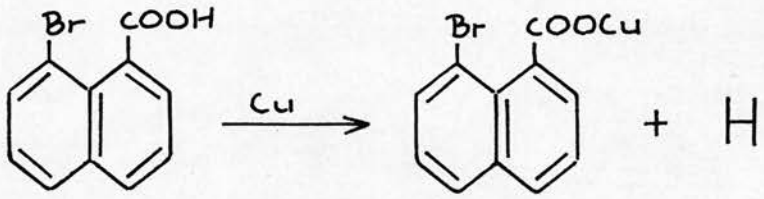


Pursell (Thesis, Edinburgh 1933) studied the debromination of o-, m-, and p - halogenated benzoic acids and of halogenated 1-naphthoic acids, work on the latter also being described by Rule, Pursell, and Brown. (J., 1934, 168). They found that treatment with copper bronze in boiling toluene removed halogen atoms in the ortho and peri positions respectively, but halogen atoms in other positions were unaffected.





Pursell suggested from experimental evidence that the hydrogen for reduction was produced by a reaction between the carboxylic acid and the copper :-



In the present research, 4:11- dibromo-:fluoranthene/

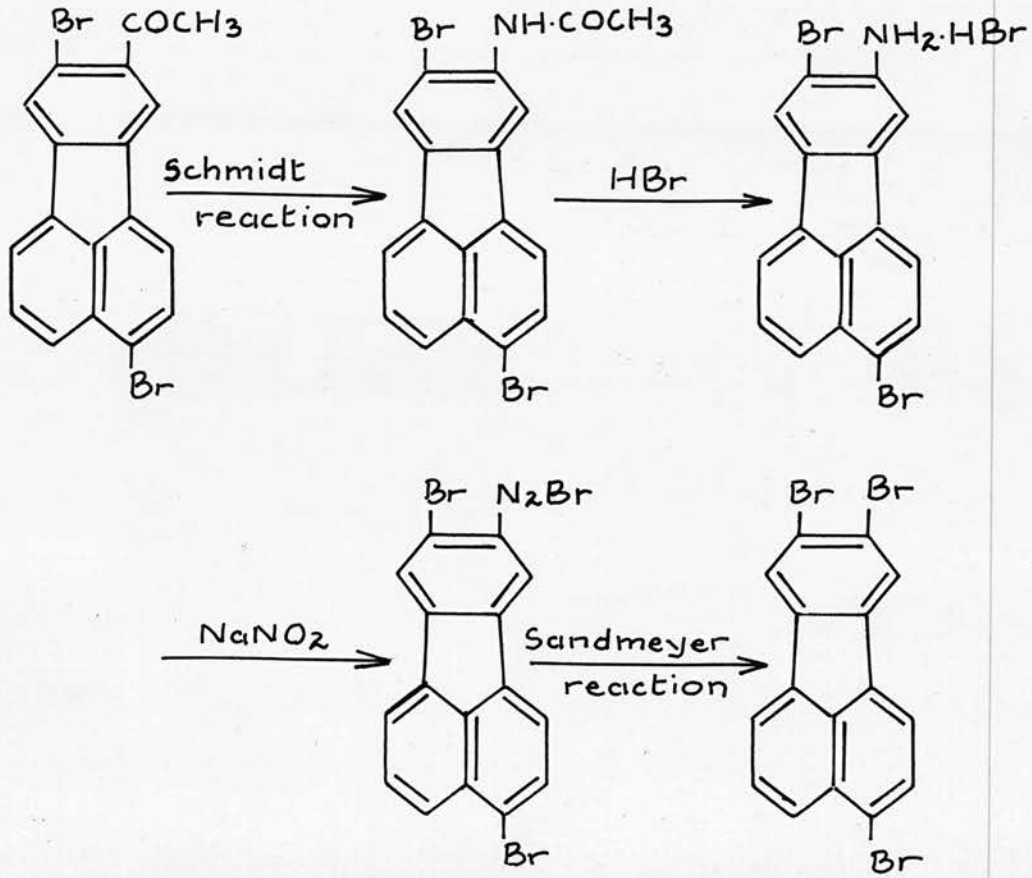
:fluoranthene -12- carboxylic acid was boiled with toluene and copper bronze but did not;give the expected 4-bromofluoranthene-12-carboxylic acid. The former acid is much less soluble than the acids investi-:gated by Pursell and it is also noteworthy that its sodium salt is almost insoluble. Thus it may be that the reaction between the copper and the carboxylic acid group does not readily take place. Pursell's work suggests that addition of molecular hydrogen may give the required dehalogenation, but the matter was not further investigated.

Tobler, Holbro, Sutter, and Kern (Helv. Chim. Acta, 1941, 24, 100E) described the preparation of a tribromofluoranthene, m.p. 205°, by the bromination of 4:11- dibromofluoranthene in nitro-benzene, and could find no evidence for the existence of the tribromofluoranthene, m.p. >345°, claimed by Goldschmiedt (Monatsh., 1880, 1 221) to result from brominating fluoranthene in acetic acid.

In the acetylation of 4:11- dibromo-fluoranthene, described previously, the small amount of 4:11- dibromofluoranthene recovered from the reaction mixture was found to contain a small amount of a substance which was possibly the tribromofluoranthene described by Goldschmiedt.

An /

An attempt was made to convert 4:11-dibromo -12- acetylfluoranthene into 4:11:12-tribromofluoranthene in order to compare the latter with the two tribromofluoranthenes mentioned above. The reaction scheme was similar to that used for the conversion of 4:12- diacetylfluoranthene into 4:12-dibromofluoranthene.



4:11- Dibromo- 12- acetylfluoranthene was readily converted by the Schmidt reaction, with sodium azide in trichloroacetic acid, into 4:11- dibromo- 12- acetamidofluoranthene. Hydrolysis of the latter with constant boiling hydrobromic acid gave the amine hydrobromide, treatment of which with aqueous ammonia liberated 4:11- dibromo 12- amino- :fluoranthene.

The diazotisation of 4:11- dibromo- 12- aminofluoranthene by suspending the hydrobromide in hydrobromic acid and treating with aqueous sodium nitrite was unsuccessful. A successful diazotisation was performed by the method of Hodgson and Walker (J., 1933, 1620). The subsequent Sandmeyer reaction, however, gave a mixture thought to be 4:11:12- tribromofluoranthene and 4:11:12:x-tetrabromofluoranthene. A sample which analysed for tetrabromofluoranthene was isolated but no tribromofluoranthene was obtained, although an analysis was obtained which indicated a mixture of the two compounds. It is thought that tribromo- :fluoranthene was formed, as planned, but this was further brominated by direct substitution, the free bromine for the reaction arising from the oxidation of hydrobromic acid by the concentrated sulphuric acid used at the diazotisation stage.

$$H_2SO_4 + 2HBr \rightleftharpoons Br_2 + SO_2 + H_2O$$

The /

The formation of bromine in this reaction is accelerated by warming, so that it is thought that repetition of the Sandmeyer reaction at a lower temperature than that used in the present experiments (the mixture was increased from 15° to 60° before dilution) would give tribromo-:fluoranthene without bromination to tetrabromo-fluoranthene.

One sample of the tetrabromofluoranthene had m.p. 223-228° after several recrystallisations Another sample, however, which was crystallised only once after chromatographic purification had m.p. 210-245° and yet analysed for tetrabromofluoranthene. Before analysis, it was thought that the first sample would prove to be tribromofluoranthene and the second would have an analysis approaching that of tetrabromofluoranthene. The identical analyses of these samples having different melting points suggests that there may even be two tetrabromofluoranthenes in the mixture from the Sandmeyer reaction.

Tobler, Holbro, Sutter and Kern (Helv. Chim. Acta, 1941, 24, 100E) prepared a tetrabromo-:fluoranthene whose high melting point of 312° indicates that it is probably different from the tetrabromofluoranthene described above.

EXPERIMENTAL.

In the following section all yields are reported as the percentage of the theoretical yield. Melting points were determined by the capillary tube method (Campbell, "Qualitative Organic Chemistry" p. 7). The apparatus was calibrated by determining the melting points of pure substances and the melting points recorded are the corrected ones. Actually, only melting points above 200° required correcting. In the case of all important reference compounds, and in most other cases, the melting points were checked by the use of a Kofler micro melting point apparatus. (Kofler, Mikrochem, 1934, 15, 242). Fluorescence observations were made in ultra-violet light generated by a Hanovia lamp. Analyses were performed by Drs. Weiler and Strauss, Oxford.

A. THE ACETYLATION OF FLUORANTHENE, AND SUBSEQUENT REACTIONS.

The acetylation of fluoranthene

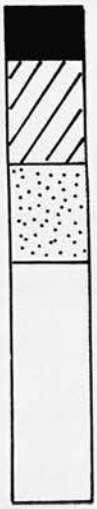
cf. Campbell and Easton. (J., 1949, 340)

The experimental procedure was different to Campbell and Easton's in that acetyl bromide was used instead of acetyl chloride and twice the molar quantity and a longer reaction time was used in an attempt to obtain a higher yield of diacetylfluoranthene.

Fluoranthene (24·0g., 0·125 mols) was dissolved in carbon disulphide (100ml.) and acetyl bromide (20ml., 0·25 mols.) was added. Powdered anhydrous aluminium chloride (45g., 0·34 mols.) was added over one hour to the stirred solution at 0°. The mixture was stirred for 72 hours and allowed to increase to room temperature over the first few hours. The mixture was decomposed with concentrated hydrochloric acid (100ml.) at 0°, the carbon disulphide was boiled off using a steam bath, and the remaining slurry was diluted with water and boiled with benzene to dissolve up the solid material. The benzene layer was separated off, washed with water, dried over anhydrous sodium sulphate, evaporated to give a sticky yellowish-brown solid. This material was crystallised from benzene to give a yellow solid, (11·0g.)m.p. 80-100°.

This/

This crystallised portion was dissolved in benzene and chromatographed on a column of alumina 24" x 1" diam. The column was developed with a 3:1 mixture of benzene and light petroleum (80-100°) and the eluted fractions were distilled and evaporated to dryness



7. Dark brown.

6. Dark yellow. Dull greenish-yellow in u.v. light.

2,3,4. Pale yellow. Greenish-yellow in u.v. light.

1. Colourless. Blue fluorescence in u.v. light.

Details of fractions are as follows:-

Fraction	Wt.g.	m.p°C	REMARKS
1	0·08	100-105	Blue fluorescence in U.V. light. Mixed m.p. indicated fluoranthene
2 3 4	0·33 0·36 0·92	68-80) 78-88) 72-94)	Pale yellow solid. Thought to be mixture of mono-acetylfluoranthenes
5	0·20	-	Interzone. Yellow syrup. Discarded
6	8·34	127-130	Dark yellow prisms. Strongly adsorbed. Cryst. from benzene to 128-132° (6·65g) Recryst from benzene to 136-138° (4·04g.) Recryst from benzene to 138-140° (3·46g.) Mixed m.p. with diacetyl-fluoranthene gave no depression.

Fraction	Wt.g.	m.p.°C.	REMARKS
7	0·12		Brown resin extracted from column with acetone

The mother liquors from the original crystallisation were similarly chromatographed to give the following fractions.

Fraction	Wt.g.	m.p.°C.	REMARKS	
1	0·09	-	Blue fluorescence. Sticky Assumed to be fluoranthene	
2	0·33	94-120	Pale yellow elongated prisms	Thought to be monoacetyl-:fluoranthenes
3	2·51	80-85	Pale yellow elongated prisms Cryst. from MeOH to give the following fractions in order of increasing solubility. 1. 83-85° 2. 83-92 3. 118-120.	
4	3·44	83-85	Pale yellow elongated prisms	
5	2·91	99-101	Pale yellow plates Cryst. from MeOH to give 99-101° (1·57g). Mixed m.p. with 11- acetyl-:fluoranthene gave no depression.	
6	-	-	Benzene solution upon boiling to /	

Fraction	Wt.g.	m.p.°C.	REMARKS
6	-	-	Benzene solution upon boiling to low volume deposited 8·08g dark yellow prisms 138-140° Mixed m.p. with diacetyl-:fluoranthene gave no depression.
7	-	-	Orange resin extracted with acetone.

Treatment of diacetylfluoranthene liquors.

The mother liquors obtained from fractions 6 from the above two columns were evaporated to low volume and chromatographed on a column of alumina 20" x 5/8" the column being developed with a 3:1 mixture of benzene and light petroleum (80-100°)

The lower pale yellow zone gave 0·53g. of sticky yellow material which could not be crystallised satisfactorily

The strongly adsorbed dark yellow zone was extruded from the column and eluted with acetone The solution gave a yellow solid which was subjected to methanol extraction and several crystallisations from benzene to give 1·53g. m.p. 137-139°. Mixed melting point with diacetylfluoranthene gave no depression.

Treatment of mono-acetylfluoranthene mixtures.

The /

The mono-acetylfluoranthene mixtures were separated by chromatography followed by crystallisation into two isomers one of which was 4-acetylfluoranthene and the other was later proved to be 11- acetylfluoranthene. Chromatography was never performed with more than about 3g of material, this amount requiring a column 24" x ¾". Development with 3:1 benzene-light petroleum (80-100) resulted in a column having the following appearance

Pale yellow. Bluish-yellow fluorescence in ultra-violet light.

Darker yellow. Dull greenish-yellow in u.v. light.

The two zones never parted and the materials obtained from each zone often required chromatographing further and always considerable crystallisation.

After several recrystallisations from alcohol, the solid from the upper pale yellow zone gave the compound later shown to be 11- acetylfluoranthene. It was easier to obtain in a relatively pure state than was 4-acetyl-:fluoranthene and consisted of flat, pale yellow, prisms /

prisms having a bluish yellow fluorescence in ultra violet light. The following materials were obtained, mixed melting points with the mono-acetylfluoranthene, m.p. 101-102°, obtained by Campbell and Easton being satisfactory.

0·21g	98-101°
0·24g	98-100°
1·29g	96-100°
0·15g	96-102°
0·45g	93-100°
0·12g	94-98°
1·46g	

After several recrystallisations from alcohol after alcohol often with the addition of a little benzene, the material from the lower darker yellow zone gave 4-acetylfluoranthene. The following materials were obtained, mixed melting points with Campbell and Easton's 4-acetylfluoranthene giving no depression

0·12g	130-133°
0·13g	129-132°
0·10g	128-131°
0·25g	128-130°
0·59g	124-130°
0·06g	124-126°
0·06g	124-128°
1·31g	

Summary of products.

Unchanged fluoranthene from 24·0g = 0·2g
Diacetylfluoranthene = 13·07g > 137° = 36·9% th.yield
11-acetylfluoranthene = 4·03g > 93° = 13·3% th.yield
4-acetylfluoranthene = 1·31g > 124° = 4·4% th.yield

The /

The above figures do not represent accurately the relative amounts of mono-acetyl-:fluoranthenes formed in the reaction since the 4-isomer is more difficult to isolate than the 11-isomer.

2:4-Dinitrophenylhydrazone of 4:12-diacetylfluoranthene

2:4-Dinitrophenylhydrazine (0·10g) was dissolved in warm concentrated sulphuric acid (0·2ml) and alcohol (2ml.) was added. To this solution was added 4:12- diacetylfluoranthene (0·10g) in hot alcohol (10ml.). An orange precipitate separated immediately and was filtered off, washed with alcohol and dried. The product sublimed at approx. 280° to yellow needles which decomposed at approx. 315° (some solid present even at 350°). After extraction with boiling acetic acid, followed by boiling alcohol, the remaining solid was crystallised from nitro-:benzene to give orange micro needles which decomposed at 320° (sublimed approx. 280°. Some solid was present even at 350°)

Analysis Found N, 12·0%

bis-2:4- dinitrophenylhydrazone requires: N, 17·3%
mono-2:4- dinitrophenylhydrazone requires: N, 12·0%

Conclusion. It appears as if only one of the carbonyl groups in 4:12- diacetylfluoranthene reacts /

reacts readily with 2:4- dinitrohpenylhydrazine by Brady's method.

2nd Acetylation of fluoranthene

A Friedel-Crafts reaction on 20·0g fluoranthene (0·10mols.) using 24·6g acetyl bromide (0·20mols.) and 36g powdered anhydrous aluminium chloride (0·27mols) and a reaction time of only 24 hours gave the following results.

Unchanged fluoranthene = 3·31g = 16·8%
Diacetylfluoranthene = 3·47g = 12·2% th. yield
11- acetylfluoranthene = 1·49g = 6·2% th. yield
4 -acetylfluoranthene = 0·62g = 2·6% th. yield

The acetylation of 4-acetylfluoranthene

4-acetylfluoranthene (1·02g., 0·0042mols.) was dissolved in carbon disulphide (10ml.) and acetyl bromide (0·8ml., 0·01mols.) was added. With the mixture stirred at 0°, powdered anhydrous aluminium chloride (1·8g., 0·014mols.) was added in small quantities over one hour and the temperature was then allowed to increase to room temperature. Stirring at room temperature was continued for 72 hours and the mixture was then poured into concentrated hydrochloric acid (20ml.) at 0°. The carbon disulphide was distilled off using a steam bath and the remaining mixture was extracted with hot benzene. The solution was washed with water, dried over anhydrous sodium sulphate distilled to low volume, and finally chromatographed on a column of alumina 17" x $\frac{1}{2}$". The column was developed /

developed with a 3:1 mixture of benzene and light petroleum (80-100°) until the lower yellow zone was completely eluted, after which the column was drained, extruded, and the dark yellow zone was eluted with acetone.

Dark brown. Discarded.

3. Dark yellow. Dull greenish-yellow in u.v. light.

2. Colourless.

1. Pale yellow. Slightly greenish yellow in u.v. light.

1 The pale yellow gave a pale yellow solid (0·02g.), m.p. 115-125, which was assumed to be unchanged 4-acetylfluoranthene.

2 The colourless zone gave no solid

3 The dark yellow zone gave yellow plates (0·74g.), m.p. 137-140°. These crystals were crystallised from methand-acetic acid mixture to give 0·61g, m.p. 140-142. A mixed melting point with diacetylfluoranthene gave no depression

Conclusion

The acetylation of 1·02g 4-acetyl-:fluoranthene gave 0·74g diacetyfluoranthene = 62% th. yield /

The acetylation of 11-acetylfluoranthene.

11- Acetylfluoranthene = 2·05g = 0·0084mols
Carbon disulphide = 10ml.
Acetyl bromide = 1·6ml. = 0·02 mols.
Anhydrous aluminium chloride = 3·6g = 0·028mols

The experimental procedure was the same as that described for the acetylation of 4-acetyl-:fluoranthene. The dried benzene solution obtained was chromatographed on a column of alumina 28" x ¾" and the column was developed with a 3:1 mixture of benzene and light petroleum (80-100°). After development, the column had the following appearance and was extruded, cut into sections, and each section was eluted with acetone, the solutions being distilled and evaporated to dryness.

3. Very dark brown. Discarded.

2. Dark yellow. Dull greenish-yellow in u.v. light.

1. Pale yellow.

1 The pale yellow zone gave 0·49g. m.p. 90-100° which were crystallised from methanol to 0·29g m.p. 97-101°. A mixed melting point with 11-acetylfluoranthene gave no depression.

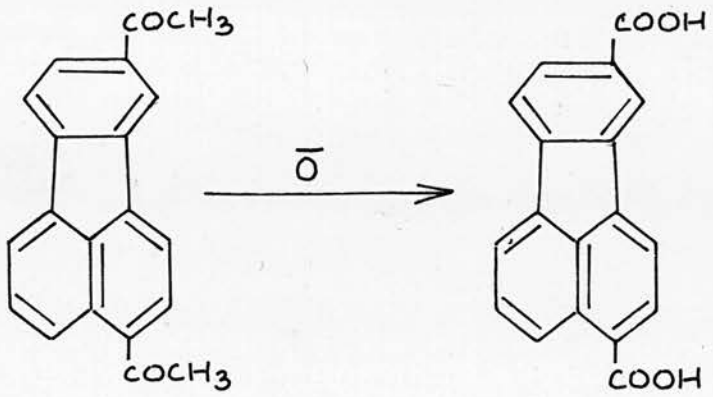
2 The dark yellow zone gave 1·29g crystals m.p. 124-134° which were further chromatographed on a column of alumina 16" x ½" to give 0·83g m.p.

132/

132-136°. Crystallisation of the latter material from a mixture of methanol and acetic acid gave 0·61g. m.p. 138-140°, not depressed when mixed with diacetylfluoranthene

Conclusion. The acetylation of 11-acetylfluoranthene (2·05g) gave 0·83g of moderately pure diacetyl-:fluoranthene = 35% yield. 0·49g. 11 acetyl-:fluoranthene were recovered.

The oxidation of diacetylfluoranthene



(a) Alkaline permanganate oxidation

Diacetylfluoranthene (1·00g) was boiled under reflux with a solution of potassium permanganate (2·92g = theoretical amount) in water (75ml.) and 3 ml. 10% sodium carbonate solution. After two hours the mixture was filtered.

The precipitate was suspended in water and sulphur dioxide was passed into the suspension to dissolve /

dissolve the manganese dioxide. There remained a suspension of dark yellow crystals (0·55g.,) m.p. 140-142°, shown by mixed melting point to be unchanged diacetylfluoranthene.

The yellow filtrate was acidified with hydrochloric acid to give a gelatinous yellow precipitate which was extracted with ether and the ether solution was dried over anhydrous sodium sulphate and distilled to dryness to give a non-crystalline yellow solid which had m.p. >350° and sublimed approx. 250° to give yellow needles. Due to its low solubility the material could not be crystallised satisfactorily.

Yield = 0·31g = 30% theoretical.

An oxidation using three times the theoretical amount of potassium permanganate gave a yield of 60% theoretical.

It was thought that the product contained other acids beside fluoranthene-dicarboxylic acid, for the following reasons:-

1. Much more than the theoretical amount of permanganate was required for a reasonable yield
2. Although sublimation gave clean golden yellow needles, m.p. >350°, softening and discolouration occurred below the sublimation point.
3. Esterification of the product gave only a low yield of the dimethyl ester.

(b) /

(b) Sodium hypochlorite oxidation

cf. Fuson and Bull, Chem. Rev., 1934, 15 275; van Arendonk and Cupery, J. Amer. Chem. Soc., 1931, 53, 3184

Sodium hydroxide (20g) was dissolved in water (50ml) and the volume was made up to about 100ml. with chopped ice. The mixture was cooled in an ice-salt bath and chlorine was passed until the solution was neutral to litmus. A further 5g of sodium hydroxide in 10 ml. of water were then added to stabilise the sodium hypochlorite thus formed.

The sodium hypochlorite solution was added to diacetylfluoranthene (1·00g.) and the suspension was vigorously stirred at 65° for 6 hours by which time almost all the solid had dissolved. The yellow solution was kept overnight treated with sulphur dioxide to remove excess sodium hypochlorite (tested with acidified potassium iodide solution), and finally acidified with concentrated hydrochloric acid to precipitate a gelatinous yellow solid which was filtered off by a sintered glass funnel to give 0·82g product, m.p. > 350°, which sublimed at approx 250° to yellow needles. A further 0·12g. were obtained by extraction of the filtrate with ether. The material was analysed for fluoranthene dicarboxylic

acid /

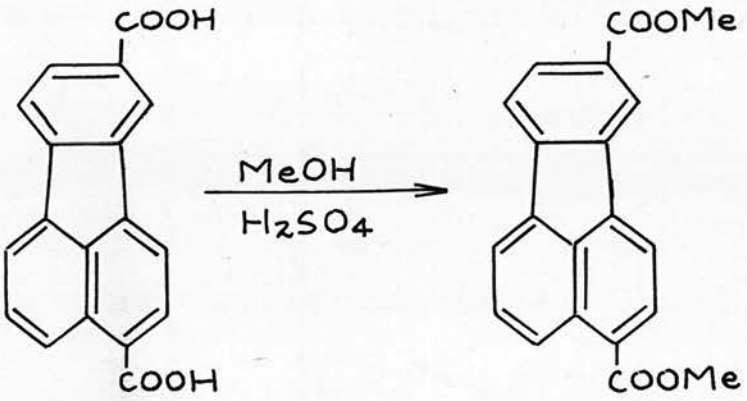
acid without further purification.

Found: C, 72·1%; H, 3·7%
Calc for $C_{18}H_{10}O_4$ C, 74·5%; H, 3·5%

Yield = 0·94g = 94% theoretical

There was no evidence of chloroform evolution during the reaction. The reaction did not appear to proceed at room temperature and was very slow below about 60°. Addition of methanol did not assist the rate of reaction

Formation of dimethyl fluoranthene 4:12-dicarboxylate



Fluoranthene dicarboxylic acid (0·43g) obtained by hypochlorite oxidation of diacetyl-:fluoranthene was boiled under reflux with methanol (150ml.) and concentrated sulphuric acid (5ml.) for 22 hours. The small amount of solid that was undissolved at the start of the reaction was completely dissolved in about 4 hours. Most of the methanol was distilled off and the remaining solution was poured into water to precipitate a gelatinous

yellow /

yellow solid which was extracted with ether to give a yellow solution having a bluish-green fluorescence. The ether solution was washed with sodium carbonate solution, washed with water, dried over anhydrous sodium sulphate and distilled to dryness to yield a pale yellow solid (0·27g) m.p. 163-178°. The ester was crystallised from a mixture of methanol and acetic acid to give a non-crystalline solid (0·13g) m.p. 175-178°. This was recrystallised from benzene to give 0·09g of m.p. 177-181°.

The recrystallised material (0·09g) was dissolved in benzene and chromatographed on a column of alumina 5" x $\frac{7}{16}$ diameter. Development with benzene gave a long pale yellow zone which was readily eluted and a small dark yellow zone which remained at the top of the column. The eluate was distilled to low volume and upon cooling deposited fine pale yellow needles (0·04g) m.p. 181-183° which were recrystallised from a mixture of methanol and glacial acetic acid to m.p. 181·5 -183° (0·03g) and analysed for dimethyl fluoranthene-dicarboxylate as follows

Found C, 75·0%; H, 4·6%

Calc for $C_{20}H_{14}O_4$ C, 75·5%; H, 4·4%

The /

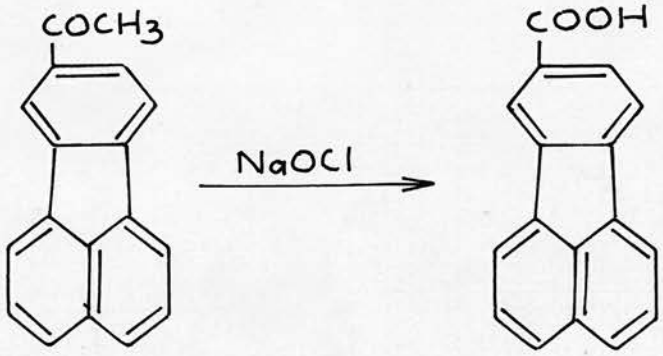
The m.p. was not depressed when the ester was admixed with the ester prepared by Campbell and Easton (loc. cit.) but gave a m.p. of 142-150° when admixed with the ester m.p. 168-169° prepared from 4:11-dibromofluoranthene by Campbell and Wilshire (J., 1951, 1404), thus showing that the substituents of the disubstituted products from the Friedel-Crafts reaction of fluoranthene are in the 4:12 positions. (See Discussion).

All mother liquors were distilled with benzene to low volume to give ultimately a benzene solution which was then chromatographed on a column of alumina 6" x $\frac{7}{16}$ to give a further quantity (0·10g) of pure ester, m.p. 181-183°.

Yield of pure product = 0·14g = 30% theoretical.

Oxidation of 11-acetylfluoranthene.

cf. Fuson and Bull, Chem.Rev., 1934, 15, 275; van Arendonk and Cupery, J. Amer.Chem.Soc., 1931, 53, 3184.



A solution of sodium hypochlorite was prepared from 10g. sodium hydroxide in the usual way (see p. 58) The solution (50ml.) was vigorously stirred at 60° whilst 11-acetylfluoranthene (0·80g) in methanol (50ml) at 60° was slowly added. Stirring at 60° was continued for 5 hours, complete solution being attained before this, and the methanol was then removed by distillation. The solution upon cooling gave a yellow precipitate (0·46g.) m.p. >350°. The filtrate was treated with sulphur dioxide to remove hypochlorite and acidified with hydrochloric acid to give an exceedingly pale yellow precipitate (0·07g), m.p. 288-290, which gave no depression of melting point when admixed with an authentic sample of fluoranthene -11- carboxylic acid.

The solid (0·46g.), m.p. >350°, gave a white residue upon ignition and was assumed to be sodium fluoranthene -11- carboxylate. It was insoluble in cold water but soluble in hot water and acidification of the solution gave an exceedingly pale yellow flocculent precipitate (0·36g.) m.p. 287-291°. A small portion was crystallised from acetic acid to m.p. 288-291°, not depressed when admixed with fluoranthene-11-carboxylic acid. It consisted /

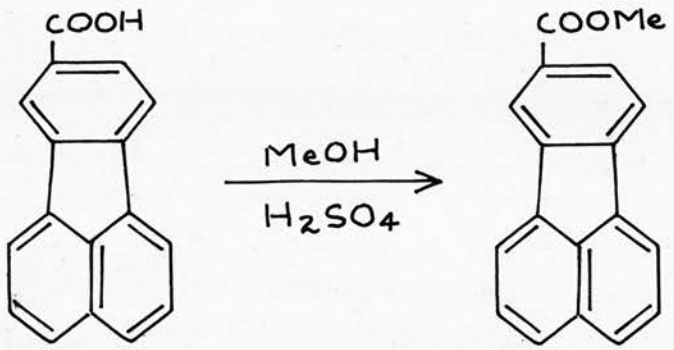
consisted of very pale yellow (almost white) clusters of needles which had a pale green fluorescence in ultra violet light. Its acetic acid solution had a blue fluorescence.

Found: C, 82·9%;H, 4·4%

Calc. for $C_{17}H_{10}O_2$ C, 82·9%;H, 4·1%

Yield = 0·43g = 54% theoretical

Preparation of methyl fluoranthene -11- carboxylate



Fluoranthene -11- carboxylic acid (0·33g) was boiled under reflux with methanol (250 ml.) and concentrated sulphuric acid (5 ml.) for 10 hours. Most of the methanol was then distilled off and the residue was poured into water to precipitate very pale yellow micro crystals (0·44g.), m.p. 92-96°. Crystallisation from methanol gave clusters of needles (0·24g.) 94-97°, which gave no depression of melting point when admixed with methyl fluoranthene -11- carboxylate.

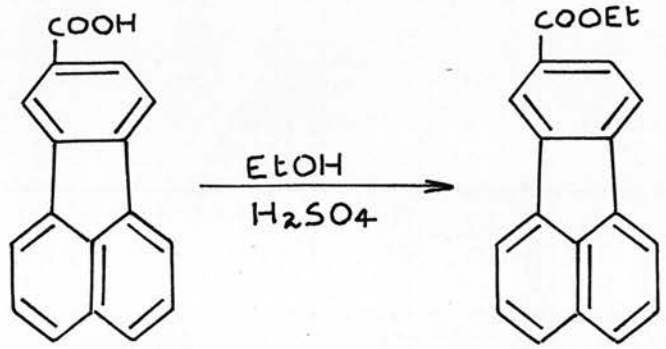
Found: C,82·8%; H, 5·0%

Calc. for $C_{18}H_{12}O_2$: C,83·1%; H, 4·7%

Yield = 0·34g. = 97% theoretical.

Preparation /

Preparation of ethyl fluoranthene -11- carboxylate



Fluoranthene -11- carboxylic acid (0·15g) was boiled under reflux with ethyl alcohol (100ml.) and concentrated sulphuric acid (4ml.) for 19 hours The solution was distilled to low volume and poured into ice water. A white emulsion formed and was left overnight to deposit a cream solid which was filtered off, washed with water, then alcohol, and dried to give to give a cream powder (0·15g.), m.p. 89-92°.

The solid was crystallised from light petroleum (60-80°) to give small cream plates (0·11g.), m.p. 92-94°.

A mixed melting point determined on both micro and macro scales between this product and ethyl fluoranthene -11- carboxylate (m.p. 94-96°), synthesised by Tucker and Whalley (J., 1949, 3213), who kindly gave us a sample, gave the value 94-96°.

Field /

Yield = 0·11g = 66% theoretical

Decarboxylation of fluoranthene -4:12- dicarboxylic acid

All fluoranthene -4:12- dicarboxylic acid used in decarboxylation experiments was prepared by the hypochlorite oxidation of 4:12- diacetyl-:fluoranthene but different batches were used in the experiments.

Fluoranthene -4:12- dicarboxylic acid (0·76g.) was heated in quinoline (15ml.) with a little copper bronze. Evolution of carbon dioxide occurred at about 150° but nevertheless the temperature was increased to 220° (as described by Campbell and Easton, loc. cit.) for one hour and the mixture was poured into dilute hydrochloric acid to yield a dark brown precipitate. This was entracted with ether to leave some black material. The yellow ether solution, which had a bluish-green fluorescence was washed with water, dried over anhydrous sodium sulphate, and distilled to dryness to yield a yellow solid (0·41g.), m.p. 150-270.

Assuming the product.to be a monocarboxylic acid, it was esterified by boiling with methanol (150ml.) and concentrated sulphuric acid (3ml.) and worked up in the usual way. The crude material was dissolved/

dissolved in benzene and chromatographed on a column of alumina 7" x ½" diameter. The column was developed with a 3:1 mixture of benzene and light petroleum (80-100°).

Dark brown
Dark yellow

3. Colourless.

2. Pale yellow. Blue fluorescence in u.v. light.

1. Colourless. Blue fluorescence in u.v. light.

1. gave <0·01g.

2. gave a sticky yellow solid (0·30g), m.p. 70-80°, which was crystallised from methanol to give an almost white solid (0.05g) m.p. 80-97°. All the material from this fraction was rechromatographed on a column of alumina 7" x ½ diameter to give very pale yellow crystals, almost white, (0·17g) m.p. 100-104°. The crystals had a greenish blue fluorescence in ultra violet light and admixture with fluoranthene gave no depression in melting point. Purification by crystallisation confirmed that the material was fluoranthene.

3. gave a very sticky yellow solid (0·07g) which started to melt below 60°. The material was rechromatographed but gave only an exceedingly sticky /

sticky yellow solid, m.p. 64-70°, which could not be purified.

Conclusion. The decarboxylation of fluoranthene -4:12- dicarboxylic acid gave fluoranthene in a yield of 32% theoretical.

Note: These decarboxylation experiments were actually performed before fluoranthene -11- carboxylic acid had been prepared. Consequently, the low solubility of this acid in organic solvents was not realised and it may be that some fluoranthene -11- carboxylic acid was present in the crude decarboxylation product but was not extracted prior to esterification.

Repeated decarboxylation of fluoranthene -4:12- dicarboxylic acid

The dicarboxylic acid (0·08g) was heated with copper bronze and quinoline as before. Formation of the ester of the product was not attempted. The ether solution gave a brownish yellow amorphous solid (0·07g). A micro melting point showed this sublimed to pale yellow elongated prisms, m.p. 265-273. Crystallisation from acetic acid gave a pale yellow non-crystalline solid, (0·03g) m.p. 268-276°. A Beilstein's test was negative. A mixed melting point with Campbell and Easton's fluoranthene -11- carboxylic acid gave no depression.

A mixed/

A mixed melting point with their fluoranthene-4-carboxylate was 230-255°. Mixed melting points were determined on both micro and macro scales.

Further purification by recrystallisation from acetic acid was attempted but was unsuccessful After almost all the crystals had melted at 276° there always remained some greenish-yellow solid m.p. >350° which was probably fluoranthene -4:12-dicarboxylic acid.

Repeated decarboxylation of fluoranthene -4:12-dicarboxylic acid

The dicarboxylic acid (0·90g) was heated at 170° for half an hour with quinoline (20ml) and a small amount of copper bronze. The mixture was worked up in the usual way to yield 0·71g. product, m.p. 260-350°. This was esterified in the usual way and a benzene solution of the crude methyl esters was chromatographed on a column of alumina 12" x $\frac{7}{16}$". The column was developed with a 3:1 mixture of benzene and light petroleum (80-100°) and finally with benzene alone.

4. Dark brown.

3. Yellow. Greenish colour in U.V. light.

2. Colourless

1. Colourless. Bluish-green fluorescence in u.v. light.

1. Gave a yellow solid (0.03g.) which was crystallised from Methanol to give a pale yellow flocculent solid (0.01g.) m.p. 240-260. Beilstein's test for halogen was positive.

2. Gave a sticky yellow material (<0.01g.)

3.(a) The benzene eluate of this zone was distilled to low volume with methanol and the solution, upon cooling, deposited a pale, greenish yellow flocculent solid (0.09g.) m.p. 155-177°. The mother liquors gave a further 0.03g. The solid was non-crystalline but clean in appearance. Recrystallisation from acetic acid - methanol mixture gave m.p.170-180°(0.05g) Further recrystallisation gave m.p. 171-183°(0.03g). The material had much too high a melting point a be a methyl fluoranthene monocarboxylate and mixed melting point determinations showed it was not dimethyl fluoranthene - 4:12 - dicarboxylate. Beilstein's test for halogen was positive, and a sodium fusion test indicated the prescence of chlorine.

(b) After material (a) had been eluted with benzene the column still had a yellowish appearance and so was extruded and so was extruded and eluted with acetone to give a pale greenish yellow flocculent solid (0.10g) m.p. 154-166°. 0.07g. of this material was rechromatographed on a column of alumina 6" x $^{7}/_{16}$", benzene being/

being used as solvent and developer. The benzene eluate was distilled to low volume with methanol to deposit 0.04g. m.p., 140-170°. The mother liquors gave a further 0.02g., m.p. 164-180°. Recrystallisation from acetic acid - methanol mixture gave m.p. 174-190° (very indefinite). Beilstein's test for halogen was positive.

4. This zone could not be extracted by acetone, benzene, or methenol but was readily extracted with sodium hydroxide solution to give an orange solution from which a gelatinous orange solid (0.04g.)., m.p. 200-320 was precipitated by acidifying with hydrochloric acid.

Attempted decarboxylation of fluoranthene - 11 - carboxylic acid.

cf. Campbell and Easton (loc.cit.)

A sample of pure fluoranthene-11-carboxylic acid was prepared by hydrolysing its methyl ester, m.p. 93-96, by boiling for 1 hour with 10% aqueous sodium hydroxide and treating the solution in the usual way.

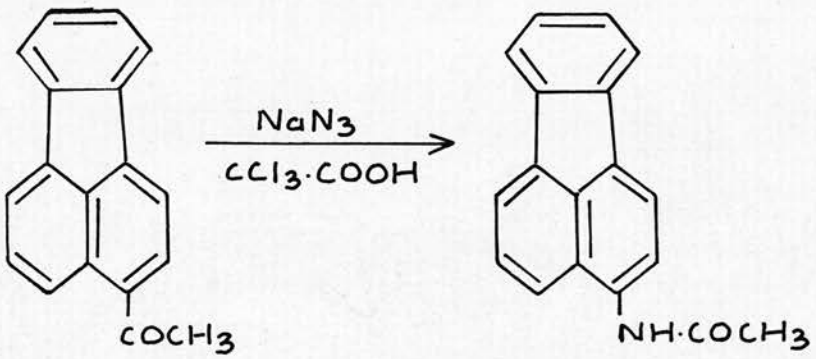
The acid (0.14g.) m.p. 287-290°, was heated in quinoline (5ml.) with a little copper bronze. Bubbles of gas were evolved at 160 but the mixture was maintained at 220° for 1 hour. Evolution of bubbles ceased after 20 minutes. The mixture was poured into 50% aqueous hydrochloric acid to precipitate a pale yellow/

yellow solid (0.14g.) This sublimed to pale yellow needles, m.p. 255-270. The solid was boiled with benzene, in which it was only slightly soluble. Upon cooling, a pale yellow solid, m.p. 270-284°, was deposited and was filtered off. The filtrate was chromatographed on a column of alumina 12"x½", using benzene, as solvent and developer, to give a firmly adsorbed yellow band at the top of the column and a lower colourless zone with blue fluorescence. This lower zone gave <0.01g. of a yellow solid (yellow in U.V.light), m.p. 180-220.

There was no trace of fluoranthene and it was shown by a blank that the bubbles observed, when the quinoline solution was heated were due to an impurity in the quinoline.

Preparation of 4 - acetamidofluoranthene by the Schmidt reaction on 4 - acetylfluoranthene.

cf. Dice and Smith, J.Org.Chem.,1949,14,179.



4-acetylfluoranthene (0.38g.) was dissolved in trichloracetic acid (2.3g.) at 60° and powdered sodium azide (0.16g.) was added in small quantities over ½ hour. Small bubbles of nitrogen were evolved. The solution was maintained at 60° for 6 hours with occasional shaking and poured into water and chopped ice to precipitate a yellow solid (0.39g.) which was washed with water and dried to give m.p. 231-233°. Crystallisation from acetic acid gave pale yellow needles (0.20g.) m.p. 244-245° which had a greenish-yellow fluorescence in the solid state, but not in acetic acid solution.

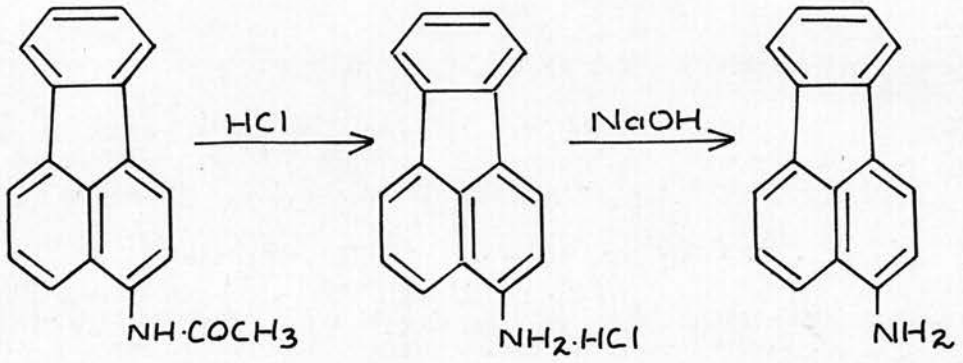
Found: N, 5.5%.

Calc.for $C_{18}H_{13}ON$: N, 5.4%.,

von Braun and Manz's 4-acetamidofluoranthene had m.p. 241-242° (Annalen, 1932, 496, 170).

Yield of pure product = 0.20g = 50% theoretical.

Hydrolysis of 4-acetamidofluoranthene to 4-aminofluoranthene.



4-Acetamidofluoranthene (0.15g.) was boiled under reflux with concentrated hydrochloric acid (5 ml.) and water (2.5 ml.) for 20 hours. The 4-acetamidofluoranthene stayed at the top of the liquid so a little alcohol was added and although this did not dissolve the solid it distributed the latter throughout the liquid, The solid gradually assumed a paler colour and the product after washing with water and drying was found to melt with decomposition at 285°.

4-aminofluoranthene has m.p.285-288°(von Braun and Manz, Annalen, 1931, 488,120).

The amine hydrochloride was boiled for 5 minutes with 5N sodium hydroxide and the yellow solid formed was washed with water and dried to give 0.12g. m.p. 111-113°. Crystallisation from a mixture of benzene and light petroleum (80-100°) gave yellow crystals, m.p. 111-113°, which were readily soluble in benzene, ether, and alcohol to give solutions having a powerful greenish-yellow fluorescence. The crystallised product was analysed as follows:

Found: N,6.3%.
Calc. for $C_{16}H_{11}N$: N,6.4%

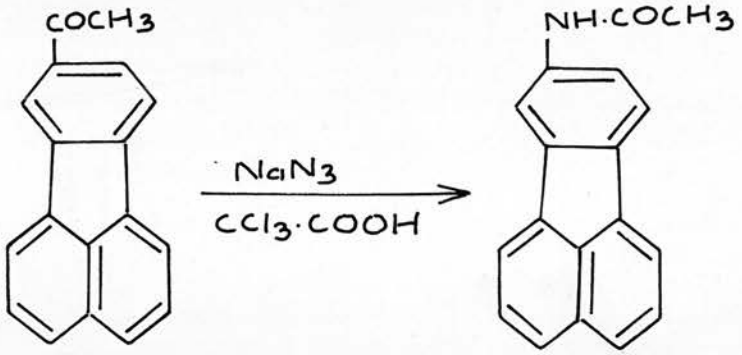
von Braun and Manz (loc.cit.) give the m.p. of 4-aminofluoranthene as 111-112°.

Yield = 0.12g.= 95% theoretical.

Preparation/

Preparation of 11-acetamidofluoranthene bythe Schmidt reaction on 11-acetylfluoranthene.

cf. Dice and Smith, J.Org.Chem.,1949,14,179.



11-Acetylfluoranthene (0.41g.) was dissolved in trichloroacetic acid (2.50g.) at 60° and powdered sodium azide (0.17g.) was added in small quantities over ½ hour. The mixture was maintained at 60° for 6 hours with occasional shaking and poured into water and chopped ice to precipitate a yellow solid which was washed with water and dried to give 0.53 g., m.p. 113-121°.

Crystallisation from benzene gave yellow crystals (0.13g.) m.p. 199-201°.

Found : N, 5.2%
Calc. for C18H13ON: N, 5.4%

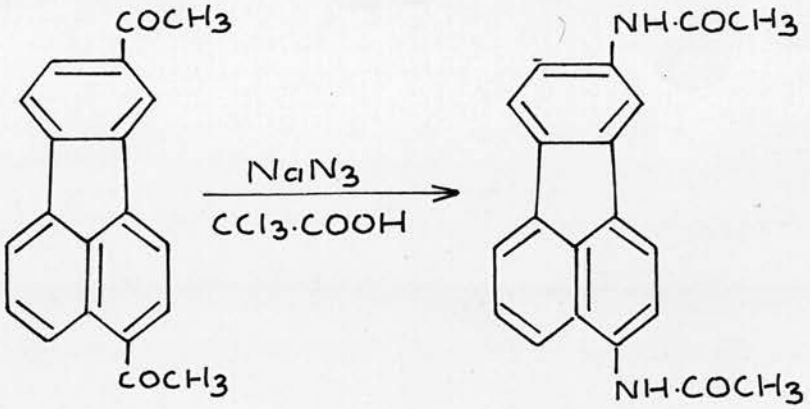
Yield= 0.13g.= 30% theoretical.

von Braun and Manz (Annalen, 1932, 496, 170) and Buu-Hoi and Cagniant (Rec.Trav.Chim., 1943,62,719) give/

give the m.p. of 11-acetamidofluoranthene as191 and 190° respectively.

Preparation of 4:12-diacetamidofluoranthene from 4:12-diacetylfluoranthene by the Schmidt reaction.

cf. Dice and Smith, J.Org.Chem.,1949,14,179.



4:12-Diacetylfluoranthene (0.38g.) was dissolved in trichloroacetic acid (4.2g.) at 60° and powdered sodium azide (0.27g.) was added in small quantities over ½ hour. After maintaining at 60° for 8 hours, with occasional shaking, nitrogen was no longer evolved and the semi-solid mixture was poured into water and chopped ice to precipitate a yellow solid which was washed with water and dried to give 0.42g., m.p. >300°.

Yield of crude product = 99% theoretical. This material was found to be pure enough for subsequent reactions.

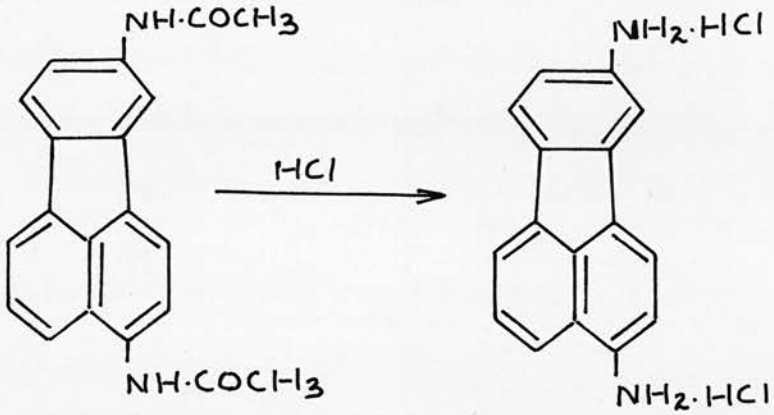
Crystallisation of a portion was attempted but was not successful due to its low solubility in the/

the many solvents tried. Purification was effected by boiling twice with alcohol to leave a yellow powder, which sublimed to yellow elongated prisms at 300° and melted at approx.370°.

Analysis:

Found: C,76.0%; H,5.1%;N,8.9%.
$C_{20}H_{16}O_2N_2$ requires: C,75.9%; H,5.1%:N,8.9%.

Hydrolysis of 4:12-diacetamidofluoranthene.



4:12-Diacetamidofluoranthene (0.19g.) was boiled under reflux with concentrated hydrochloric acid (10 ml.). The solid quickly dissolved and the solution deposited small, almost white, needles of 4:12-diaminofluoranthene dihydrochloride after ½ hour. After boiling for 2 hours, the suspension was cooled and the solid was filtered off, washed with concentrated hydrochloric acid followed by dry ether and air dried to give very pale buff needles (0.16g.), m.p. > 300°.

Analysis: Found: N,8.9%; Cl,22.8%
$C_{16}H_{14}N_2Cl_2$ requires: N,9.2%; Cl,23.2%
Yield = 0.16g = 88% theoretical.

Similarly,/

Similarly, hydrolysis with hydrobromic acid (34%) gave 4:12-diaminofluoranthene dihydrobromide.

Liberation of the free diamine.

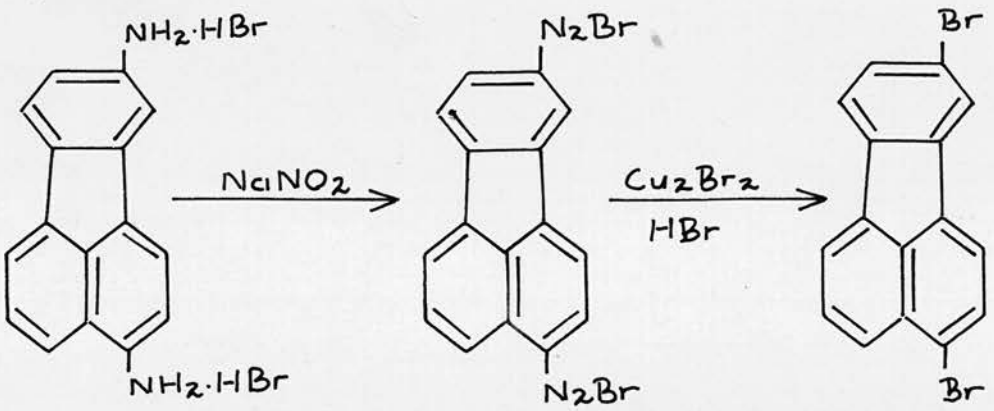
When aqueous ammonia (20ml.,0.880) was added to 4:12 diaminofluoranthene dihydrochloride the colour of the latter changed to dark yellow but the solid rapidly gave a brown resinous solid. The suspension was boiled for 1 hour, filtered, and the solid was washed with water and dried. Crystallisation from benzene was attempted (solution had strong greenish-yellow fluorescence) but was not very successful. The material came down as a brown powder, m.p.approx. 100-115°.

A hot saturated solution of picric acid in benzene was added to a hot benzene solution of the crude diamine to give an immediate reddish-brown precipitate, m.p. 210-215°(decomp.). Recrystallisation from benzene (not very soluble) gave reddish-brown micro-crystals, m.p. approx. 210-220° (decomp.). A further recrystallisation gave no improvement of melting point.

Analysis: Found:N,14.5%.
Picrate $C_{22}H_{15}O_7N_5$ requires:N,15.2%.

Preparation of 4:12-dibromofluoranthene by the Sandmeyer reaction./

Preparation of 4:12-dibromofluoranthene by the Sandmeyer reaction.



4:12-Diaminofluoranthene, prepared from 4:12-diacetylfluoranthene (2.00g.), was suspended in 34% hydrobromic acid and tetrazotised at 0° by a slight excess of 20% aqueous sodium nitrite. The solution (which gave a purple precipitate with alkaline β naphthol solution) was filtered and added slowly to a solution of freshly prepared cuprous bromide (1.1g.) in 34% hydrobromic acid (3 ml.) at 0° to give a dark brown precipitate. The mixture was allowed to slowly attain room temperature, increased to 60° over ½ hour, and finally boiled. The resulting black precipitate was washed with water, dried, and extracted first with chlorobenzene and then with benzene. The combined extracts were chromatographed on a column of alumina 12" x ½", using benzene to develop the column.

Dark brown. Discarded.

3. Orange.

2. Yellow.

1. Pale yellow.

1. The pale yellow zone, which was eluted with benzene, gave an orange-yellow solid (1·09g.) which was rechromatographed, using benzene as solvent and developer, to give a uniformly pale yellow band which was eluted with benzene to give the following fractions:

(a) 0·10g., m.p. 156-164°. Crystallisation from methanol-acetic acid mixture gave pale yellow elongated prisms, m.p. 162-165°, which gave a mixed melting point of 144-152° when admixed with 4:11- dibromofluoranthene

Analysis: Found: C,52·6%;H,2·1%Br,44·7%.
$C_{16}H_8Br_2$ requires: C,53·4%:H,2·2%:Br,44·4%.

(b) 0·19g. m.p. 152-164°. This material was crystallised from benzene to m.p. 159-165°(0·07g.) and recrystallised from benzene to m.p. 162-165°(0·01g.).

Analysis: Found: C,53·4%:H,2·6%:Br, -
$C_{16}H_8Br_2$ requires: C,53·4%:H,2·2%:Br,44·4%.

(c) 0·19g. m.p. 153-163°. This material was crystallised from benzene to m.p. 156-164° (0·13 g.) and recrystallised to 159-164°(0·08g.) A further recrystallisation from benzene gave m.p. 162-165° (0·02g.)

2. The darker yellow zone, which was eluted with benzene gave a sticky orange-yellow solid (0·04g.)

3. /

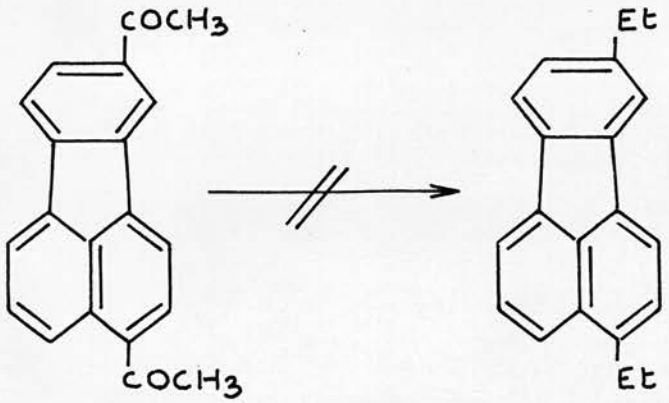
3. The orange zone was eluted with acetone after the column had been drained and extruded. The solution gave a red non-crystalline solid (0.11g.) which was not investigated.

Yield of relatively pure 4:12-dibromofluoranthene = 0.48g = 19% of the theoretical amount from 2.00g. diacetylfluoranthene.

A reaction in which 4:12-diaminofluoranthene dihydrochloride was tetrazotised in concentrated hydrochloric acid and added to cuprous bromide in hydrobromic acid and was also effective for the preparation of 4:12-dibromofluoranthene. (15% yield of theoretical from dihydrochloride).

Reduction of 4:12-diacetylfluoranthene by the modified Wolff-Kishner method.

cf. Huang-Minlon, J. Amer. Chem. Soc., 1946, 2867.



4:12Diacetylfluoranthene (1.00g), potassium hydroxide (4.50g.), 100% hydrazine hydrate (2.75 ml.) and/

and ethylene glycol (6 ml.) were boiled under reflux for 1½ hours. The condenser was then removed and the temperature was allowed to increase to 195°, when the condenser was replaced and the mixture was boiled under reflux for a further 4 hours. A greenish-brown solid was formed even before the temperature had reached 195°. The cooled solution was diluted with water and acidified with concentrated hydrochloric acid and the precipitate mentioned above was filtered off, washed with water and dried to give a hard light brown solid, m.p. >300° (1.11g.). It was found impossible to purify the product by crystallisation due to its extremely low solubility.

Analysis: Found: N,12.3%
The azine requires: N, 9.9%.
The monohydrazone of diacetyl-fluoranthene requires: N,17.7%.

The hydrolysis of the product with concentrated hydrochloric acid gave lower melting material (0.45g.) m.p. 64-73. Purification of the latter by chromatography gave as the main product a yellow solid (0.15g.) m.p. 89-93 (softened at 82°) but this could not be obtained in a pure state. It was possibly crude 4:12-diacetylfluoranthene obtained by the hydrolysis of dihydrazone.

A repeat reduction of diacetylfluoranthene

using/

using 85% hydrazine (instead of 100% as above) gave no better result.

Clemmensen reduction of 4:12-diacetylfluoranthene.

Granulated zinc (5.0g.) was shaken with a mixture of water (7.5ml.), concentrated hydrochloric acid (0.25 ml.) and mercuric chloride (0.50g.). After 5 minutes the aqueous portion was decanted and the reactants added in the following order:-

4.0 ml. water
9.0 m.l. concentrated hydrochloric acid.
5.0 ml. toluene.
1.00g. 4;12-diacetylfluoranthene.
A few drops of glacial acetic acid.

The mixture was boiled under reflux for 24 hours, 3 ml. portions of concentrated hydrochloric acid being added every 3 hours. Benzene was added and the benzene layer, which had a pronounced green fluorescence, was separated off, washed with sodium carbonate solution, then water, and finally distilled to dryness to yield a yellow solid (0.92g.), m.p. 110-130°. This was dissolved in benzene and chromatographed on a column of alumina 14"x⅝", development being performed with benzene.

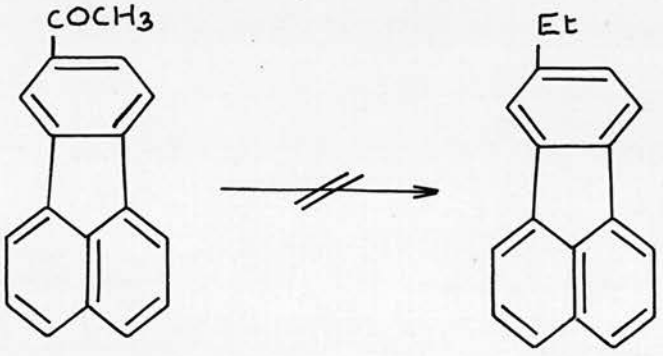
1. The pale yellow zone was readily eluted with benzene to give a sticky yellow syrup (0.09g.).

Crystallisation/

Crystallisation from methanol-benzene mixture gave a pale yellow solid, m.p. approx. 190-200° (very indefinite). This melting point is too high for the material to be diethylfluoranthene.

2. The dark yellow zone moved slowly down the column and so was eluted with acetone after the column had been drained, and extruded. The solution gave a yellow solid (0.75 g.) m.p. 125-130°. This was crystallised with difficulty from benzene-light petroleum to m.p. 127-131°. (0.30g.). Recrystallisation of 0.16g. of this material gave m.p. 138-141° (0.12g.) undepressed when admixed with 4:12-diacetylfluoranthene.

Clemmensen reduction of 11-acetylfluoranthene.

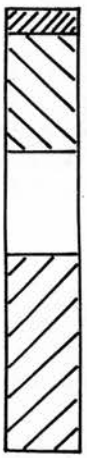


Amalgamated zinc (5g) was prepared as in the previous experiment. The reagents were added in the following order:-

4.0 ml. water
9.0 ml. concentrated hydrochloric acid.
5.0 ml. toluene.
0.72 g. 11-acetylfluoranthene.

The/

The mixture was boiled under reflux for 24 hours, 3 ml. concentrated hydrochloric acid being added every 3 hours. Benzene was added and the benzene layer was washed with water, dried over anhydrous sodium sulphate and chromatographed on a column of alumina 20"x$\frac{1}{2}$". The column was developed with a 50:50 mixture of benzene and light petroleum (40-100°).



4. Dark lime yellow. Dark yellow in u.v.

3. Pale yellow. Blue fluorescence in u.v. light.

2. Colourless.

1. Pale yellow. Greenish-yellow fluorescence in u.v. light.

1. The pale yellow zone was eluted with benzene-light petroleum to give a yellow syrup (0.59g.) which contained some yellow plates, m.p. 250-267°(softened approx.100°). The syrup was triturated with alcohol but did not solidify. It was dissolved in benzene (solution had green fluorescence even in daylight) and added to picric acid (0.50g.) in the minimum amount of hot benzene. The solution went red and, upon/

upon cooling, deposited orange crystals (0.08g.), m.p. 250-269° (melted slightly at 230°). This picrate was dissolved in benzene and chromatographed on a column of alumina 11"x½", developing with a 50:50 mixture of benzene and light petroleum (80-100°). The picrate decomposed upon the column since a uniform pale yellow zone (pale greenish yellow in U.V. light) was readily eluted with benzene to leave a strongly adsorbed dark yellow band of picric acid at the top of the column. The solution of the pale yellow zone was boiled down with alcohol and the solution, upon cooling, deposited well defined pale yellow plates (0.02g.), m.p. 273-276°, having a greenish-blue fluorescence in U.V. light.

Analysis:

Found: C,93.7%,H,5.5%

Ethylfluoranthene, C18H14 requires: C,93.9%,H,6.1%

The high melting point of the product suggests that it is not the required 11-ethylfluoranthene, but possibly 2:3-di-(11-fluoranthyl) - but - 2 - ene, C36H24, which requires C,94.7%; H,5.3.

The filtrate from the preparation of the picrate was chromatographed on a short column of alumina to remove picric acid and the benzene solution obtained was distilled to low volume with alcohol to deposit a pale yellow powder (0.07g.) m.p. 150-250°. Since this material was impure, the preparation of its picrate/

picrate was again attempted and the picrate obtained consisted of orange-yellow needles (0·05g.) m.p. 230-252°. Crystallisation from benzene gave 0·02g. m.p. 240-252° (sublimed 230° and darkened). Recrystallisation gave m.p. 240-252°(d.)

Analysis:

Found: N,11·1%

Picrate of above hydrocarbon, $C_{42}H_{27}O_7N_3$, requires: N, 6·1%

Dipicrate " " " , $C_{48}H_{30}O_{14}N_6$ requires: N, 9·2%

The mother liquors from the recrystallisation of this picrate were chromatographed on a short column of alumina to decompose the picrate and remove picric acid. The eluate was distilled to low volume with alcohol and deposited pale yellow plates (0·01g.), m.p. 265-275° (softened below this). This was the hydrocarbon as analysed previously, though less pure.

2. The colourless zone of the original column gave a sticky yellow syrup (<0·01g.).

3. The pale yellow zone gave a sticky yellow syrup (0·04g.)

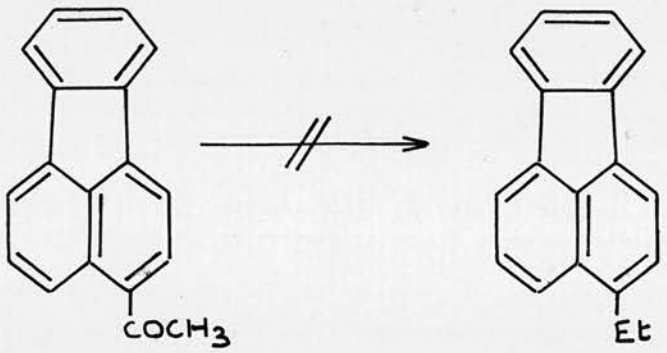
4. The dark lime yellow zone, which was strongly adsorbed, was extruded and extracted with acetone. The acetone solution had a powerful green fluorescence in daylight and U.V. light but gave only a minute amount of solid when distilled to dryness.

Conclusion:

The high melting point of the only pure product isolated from the Clemmensen reduction of 11-acetylfluoranthene /

acetylfluoranthene suggests the product is a dimer instead of the required 11-ethylfluoranthene.

Clemmensen reduction of 4- acetylfluoranthene.



Amalgamated zinc (5 g.) was prepared as before and the reagents were added to it in the following order:-

4 ml. Water
9 ml. Concentrated hydrochloric acid
5 ml. Toluene
0·45 g. 4- Acetylfluoranthene
Few drops of acetic acid.

The mixture was boiled under reflux and concentrated hydrochloric acid was added every 8 hours. After 24 hours, the toluene layer was separated off. The zinc had a yellow solid adhering to it and so was extracted with benzene to give a yellow solution having a powerful green fluorescence. The benzene and toluene solutions were combined, washed with water, dried over anhydrous sodium sulphate and chromatographed on a column of alumina 20" x $\frac{1}{2}$". Development was performed with a 50:50 mixture of benzene and light petroleum (60-80^0) to give a column having the following /

following appearance

3 and 4. Yellow. Dull greenish yellow in U.V. light.

1 and 2. Pale greenish yellow. Bluish colour in U.V. light.

Fractions were eluted with the benzene-light petroleum mixture and were distilled and evaporated to dryness.

1. The lower part of the pale greenish yellow zone gave a dark yellow syrup (0·07g.) which gave a semi-solid when triturated with alcohol. It had a green fluorescence in ultra-violet light. The material partially melted below 100°, but some solid remained even at 300° (blackened below this).

2. The upper part of the pale greenish yellow zone gave 0·10g. of material which appeared identical with 1.

3. The lower part of the yellow zone gave yellow spars (0·10g.), m.p. 115-122°. These were crystallised from alcohol to give m.p. 125-128°, undepressed when the solid was admixed with 4-acetylfluoranthene.

4. The upper part of the yellow zone gave yellow spars (0·14g.), m.p. 121-128°, which were crystallised from alcohol to m.p. 125-128°. The

m.p. /

m.p. was not depressed when the crystals were admixed with 4- acetylfluoranthene.

Fractions 1 and 2 were combined, dissolved in hot benzene (3 ml.) and a solution of picric acid (0·10g.) in hot benzene (1 ml.) was added. The solution went orange in colour and upon cooling deposited orange micro needles (0·07 g.), m.p. 305-315° (darkened and softened at 220°). These were recrystal-:lised from benzene to give orange micro needles which darkened at 235° and sublimed to pale yellow elongated prisms, m.p. 305-320.

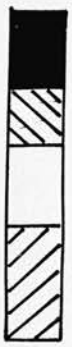
Analysis

Found: N, 10·1%

Mono-picrate of hydrocarbon $C_{36}H_{24}$ requires: N, 6·1%

Di-picrate " " " " : N, 9·2%

The picrate was dissolved in benzene and chromatographed on a column of alumina 15" x ½". After development with a 50:50 mixture of benzene - light petroleum (60-80°) the column had the following appearance.



Dark yellow (Picric acid)

Yellow. Greenish-yellow in U.V. (Probably 4-acetylfluoranthene.)

Colourless

Pale greenish yellow.

The lowest zone moved rapidly down the column and the greenish-yellow solution obtained was distilled to low volume with alcohol and upon cooling deposited a yellow powder (0·02g.), m.p. 170-270° (softened/

(softened 150°). This was crystallised from alcohol to give a yellow powder (0·006 g.), m.p. 180-290°. Despite its large melting range it was analysed.

Analysis

Found: C,92·2%; H, 5·8%

4 - ethylfluoranthene, $C_{18}H_{14}$, requires: C,93.9%; H, 6.1%

2:3-di-(4-fluoranthyl) but-2-ene, $C_{36}H_{24}$, requires: C,94·7%; H,5·3%

The high limit of the melting point range suggested that the material contained dimeric products, of the type given above, instead of the expected 11- ethylfluoranthene.

The original liquors from the preparation of the picrate were chromatographed on a column of alumina 11" x ½", a 50:50 mixture of benzene - light petroleum (60-80°) being used as developer. The main zone which was greenish yellow (greenish-blue in U.V.) gave a yellow syrup (0·07 g). This was crystallised from alcohol (solution had green fluorescence in daylight) to give m.p. 70-220°(micro). Crystallisation from light petroleum (60-80°) was unsatisfactory.

Conclusion:

Clemmensen reduction of 4-acetylfluoranthene (0·45g.) gave 53.3% unchanged material (0·24g.) and a mixture of reduction products. A pure compound could not be isolated from the latter but the high limit /

limit of the melting range suggests that reduction gave dimeric material instead of, or in addition to, the required 4-ethylfluoranthene. The fact that solid adhered to the zinc used for reduction is in agreement with the formation of polymeric material. (cf. Adams' "Organic Reactions" 1, p. 155).

B. THE ACETYLATION OF 4:11-DIBROMOFLUORANTHENE, AND SUBSEQUENT REACTIONS.

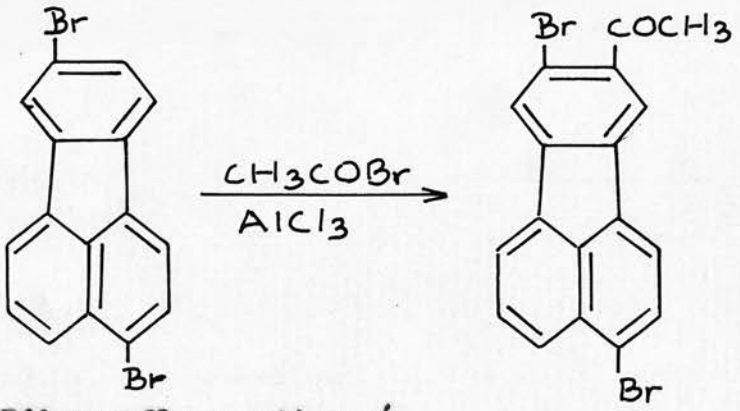
Preparation of 4:11-dibromofluoranthene.

Tobler et al. Helv.Chim. Acta, 1941, 24, 100E.

Bromine (64 ml.) in nitrobenzene (150 ml.) was dropped into a solution of fluoranthene (121g.) in nitrobenzene (900 ml.), with stirring, over a period of 2 hours. After 48 hours stirring, air was blown through the mixture to remove hydrobromic acid and the crude precipitated dibromofluoranthene was dissolved by warming the reaction mixture to 120°. Upon cooling, dibromofluoranthene crystallised out and was filtered off, pressed, and the adherent nitrobenzene was steam distilled off to leave crude 4:11-dibromofluoranthene (142g.), m.p. 192-198°. Recrystallisation from chlorobenzene gave greenish yellow elongated prisms (108g.) m.p. 201-204° (lit., 205°).

Yield = 108g = 50% theoretical.

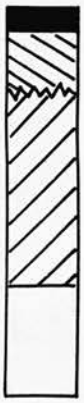
Acetylation of 4:11-dibromofluoranthene.



Dibromofluoranthene/

Dibromofluoranthene (10.0g., 0.0278 mols) was partially dissolved in carbon disulphide (50 ml.) and acetyl bromide (6.80g., 0.0556 mols) was added. With the temperature of the mechanically stirred mixture at 0°, powdered anhydrous aluminium chloride (11.0g., 0.0834 mols.) was added over ½ hour. The mixture was then allowed to attain room temperature, stirred for 72 hours, and the dark brown mixture was decomposed with ice cold concentrated hydrochloric acid. After distilling off the carbon disulphide, using a water bath, the suspension was diluted, filtered, washed with water and dried to give a light brown powder (10.93g.) m.p. 130-145.

A portion (5.04g.) of this powder was dissolved in benzene and chromatographed on a column of alumina 26"x¾" using benzene as developer.



Very dark brown.

3. Orange zone merging into yellow zone

2. Yellow.

1. Colourless but gave pale yellow solution

1. The colourless zone was eluted with benzene to give a pale yellow solution which gave pale yellow needles (0.08g.), m.p. 184-190°. Crystallisation from/

from benzene gave m.p. 195-200° which was undepressed when mixed with 4:11-dibromofluoranthene.

2.(a). The bottom of the main yellow zone was eluted with benzene and the solution was distilled to low volume to deposit pale yellow elongated prisms (0.36g) m.p. 164-165°. Recrystallisation from benzene did not alter the melting point but the sample gave a mixed melting point of 148-176° with 4:11-dibromo-fluoranthene. The sample was analysed for 4:11-dibromo-acetylfluoranthene as follows:-

Found: C,53.6%; H,2.5%; Br, 39.6%.
$C_{18}H_{10}OBr_2$ requires: C,53.8%; H,2.5%; Br,39.75%.

Evaporation of the initial mother liquors gave a further 0.10g., m.p. 154-158°.

(b). The middle of the main yellow zone was eluted with acetone and the solution was distilled to low volume to deposit 1.46g., m.p. 159-162°. The mother liquors gave a further 0.64g., m.p. 120-134°.

(c). The top of the main yellow zone was similarly treated and gave 0.41g., m.p. 148-158° and 0.77g., m.p.122-142°.

3. The orange zone was eluted with acetone and gave an orange-brown resin (0.23g) which was discarded/

discarded.

The remainder of the crude powder (5.89g). was chromatographed in an identical way to give the following fractions, the latter being numbered as before.

1. 0.27g.,m.p. 147-155° + 0.16g.,m.p.120-140°

2.(a) 0.34g.,m.p. 163-165° + 0.13g.,m.p.153-157°

(b) 1.18g.,m.p. 163-165° + 0.47g.,m.p.128-144°

(c) 1.33g.,m.p. 153-159° + 0.63g.,m.p.110-134°

(d) Dark yellow resin (0.36g.),m.p. 75-100°.

3. The orange and brown zones were discarded.

All materials with initial m.p. <153° from the above two columns were bulked together (3.70g.) and similarly chromatographed on a column of alumina 26" x $\frac{3}{4}$" to give the following fractions:-

1. The colourless zone was eluted with benzene to give a pale yellow solution which was distilled to low volume to deposit pale yellow elongated prisms (0.02g.) m.p. >360° (sublimed).

Found: Br, 56.0%.
C16H7 Br 3 requires: Br, 54.6%.

$C_{16}H_7Br_3$

(cf. the tribromofluoranthene, m.p. >345° described by Goldschmiedt (Monats.,1880, 1, 221))

The/

The mother liquors were distilled to dryness to give 0.13g., m.p. 140-150°, crystallisation from alcohol giving 0.07g., m.p. 146-178°. A small portion of low solubility had m.p. 185°-190° which was not depressed by 4:11-dibromofluoranthene.

2. (a) 0.15g., m.p. 163-165° + 0.12g.,m.p.144-154°.

(b) 1.11g., m.p. 154-159° + 0.32g.,m.p.130-145°. Recrystallisation from benzene gave 0.92g.,m.p. 162-164°.

(c) 0.15g.,m.p.126-144°. A yellow resinous solid (0.41g.),m.p.75-155° was obtained from the mother liquors.

(d) A yellow resinous solid (0.29g.),m.p.75-95°.

3. A darker yellow upper zone gave a dark yellow resinous solid (0.13g.) m.p.65-105°.

Attempts to purify the resinous materials obtained from 2(c), 2(d) and 3 were unsuccessful.

All materials within the melting range 153-165° and obtained from fractions 2 were shown to be identical by mixed melting point determinations.

Conclusion: The action of acetyl bromide on 4:11-dibromofluoranthene, in the presence of aluminium chloride, gave a 4:11-dibromo-monoacetylfluoranthene, later/

later shown to be 4:11-dibromo-12-acetylfluoranthene. A small amount of 4:11-dibromofluoranthene was recovered along with a very small amount of a substance which was possibly a tribromofluoranthene present as impurity in the original 4:11-dibromofluoranthene.

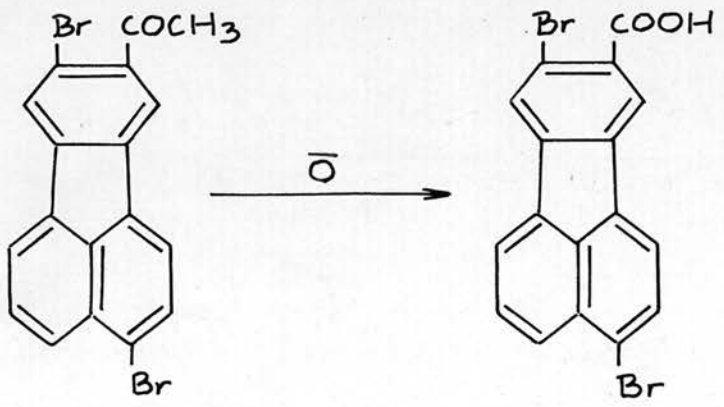
Yield of 4:11-dibromo-12-acetylfluoranthene = 6.32g. crude.
= 56% theoretical from 4:11-dibromofluoranthene.

2:4-dinitrophenylhydrazone of product.

2:4-dinitrophenylhydrazine (0.05g.) was dissolved in warm concentrated sulphuric acid (0.2 ml) and alcohol (5ml) was added. To the solution was added 4:11-dibromo-acetylfluoranthene m.p.143-150°, (0.10g.) in hot glacial acetic acid (20 ml). Upon cooling, an orange solid (0.11g.), m.p.253-270°, was deposited. This was too insoluble to be recrystallised from acetic acid or alcohol but was purified by boiling with these solvents to leave an orange, non-crystalline solid, m.p. 275-279° (micro, uncorrected).

Found: N,9.8%.
$C_{24}H_{14}O_4N_4Br_2$ requires: N,9.6%.

Oxidation of 4:11-dibromo-12-acetylfluoranthene.



(a)/

(a) Hypochlorite oxidation.

cf. Fuson and Bull, Chem.Rev.,1934,15,275;
van Arendonk and Cupery, J.Amer.Chem.Soc., 1931,53,3184.

Sodium hypochlorite solution prepared as previously described,from sodium hydroxide (10g.), was vigorously stirred at 60° whilst 4:11-dibromo-12-acetylfluoranthene (0.81g.) partially dissolved in methanol (50 ml). at 60°, was slowly added. The mixture was stirred at 60° for 3½ hours, left at room temperature overnight, and filtered to give a yellow powder (0.80g.). This started to melt at 138°, but the melting point was very indefinite, there being indication of the presence of a small amount of high melting material. The powder was insoluble in boiling water. The filtrate was treated in the usual way but gave no carboxylic acid.

Alkaline permanganate oxidation.

4:11-Dibromo-12-acetylfluoranthene (0.80g.) was boiled under reflux with potassium permanganate (0.84g. = theoretical amount) in water (50 ml.) with the addition of a little dilute aqueous sodium-carbonate. There was no purple colour remaining after 1½ hours but the mixture was boiled for 3½ hours, and filtered. The solid was suspended in water and treated/

treated with sulphurous acid to dissolve manganese dioxide and leave a yellow powder (0.67g.), m.p. 143-150°, which gave no depression with the starting material.

The yellow filtrate, upon cooling, deposited a gelatinous yellow solid, presumably a sodium salt. The mixture was boiled up again and acidified with concentrated hydrochloric acid to give a gelatinous yellow precipitate (0.07g.), which started melting at 235° but was very indefinite. Sublimation to yellow needles occurred at approx. 200°.

Sodium hypobromite oxidation.

Bromine (6.7 ml.) was added dropwise to 3N sodium hydroxide solution (93 ml.) at 0°, whilst the mixture was shaken occasionally. 4:11-dibromo-12-acetylfluoranthene (0.80 g.) was added and the mixture was stirred vigorously at 60° for 22 hours and filtered. Some white crystals were deposited in the upper part of the apparatus, well above the liquid level, but these disappeared before a melting point had been performed, (possibly carbon tetrabromide). The filtrate was steam distilled, but gave no indication of bromoform or carbon tetrabromide, and the remaining solution was treated with sulphur dioxide and acidified with concentrated hydrochloric acid but gave no precipitate/

precipitate and an ether extraction gave no product.

The solid was washed with water and dried to give a yellow powder (0.67g.) which melted at approx. 300° but darkened and softened much below this. After boiling with benzene to dissolve unchanged 4:11-dibromo-12-acetylfluoranthene, there remained a yellow powder (0.40g.), m.p. >325° (darkened 285°) which was assumed to be sodium 4:11-dibromofluoranthene-12-carboxylate since ignition gave a slight white residue, soluble in water.

The sodium salt was boiled with concentrated hydrochloric acid (50 ml.) for 2½ hours. At no stage did the solid dissolve but it went slightly paler in colour. The suspension was filtered off, washed with water and dried to give a pale yellow powder (0.35g.), m.p.300-306° (with blackening). Microscopic examination showed the material to be pale yellow needles which sublimed at approx.200°. It was only slightly soluble in benzene or acetic acid and even less soluble in alcohol. Crystallisation from benzene gave pale yellow needles, m.p. 306-308°, which were analysed for 4:11-dibromofluoranthene-12-carboxylic acid as follows:-

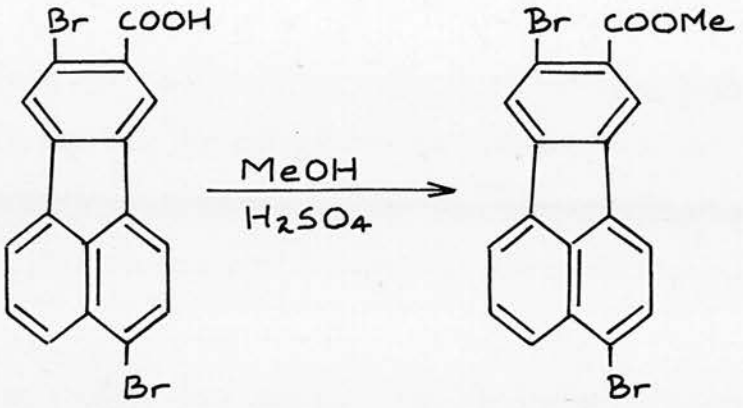
Found: C,51.0%; H,2.1%:Br,39.1%
$C_{17}H_8O_2Br_2$ requires: C,50.5%; H,2.0%;Br,39.55%
Yield = 0.35g. = 44% theoretical.

Repeated hypobromite oxidation.

Using/

Using a longer reaction time (44 hours), 4:11-dibromo-12-acetylfluoranthene (0.78g.) gave a higher yield of 4:11-dibromofluoranthene-12-carboxylic acid (0.60g.= 77%) m.p. 304-308°.

Preparation of methyl 4:11-dibromofluoranthene-12-carboxylate.



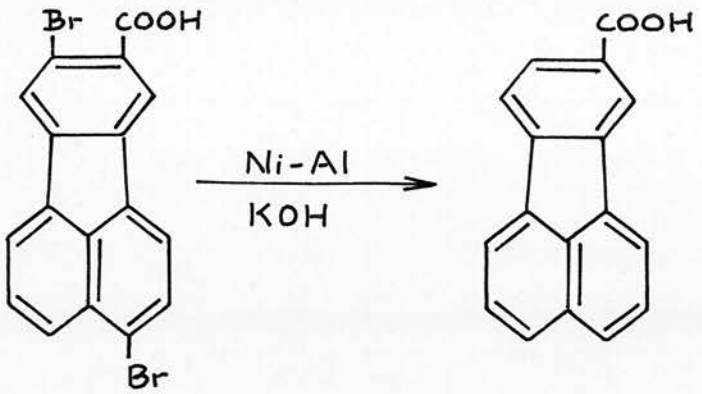
4:11-Dibromofluoranthene-12-carboxylic acid (0.30g.) was boiled under reflux with methanol (100 ml) and concentrated sulphuric acid (3 ml.) for 18 hours. Upon cooling, a pale yellow solid was deposited and was filtered off, washed with methanol, and dried to give pale yellow needles (0.25g.), m.p. 186-188°. These were chromatographed on a column of alumina, 9"x$\frac{1}{2}$", benzene being used as solvent and developer. A pale yellow zone moved rapidly down the column and yielded fine pale yellow needles (0.22g.), m.p.189-190°. A portion was crystallised from alcohol to give m.p. 190-191°.

Analysis. Found: C,51.9%;H,2.4%;Br,38.7%.
$C_{18}H_{10}O_2Br_2$ requires: C,51.7%;H,2.4%;Br,38.2%.
Yield = 0.25g. = 79% theoretical.

Debromination/

Debromination of 4:11-dibromofluoranthene-12-carboxylic acid.

Cf. Papa, Schwenk, and Ginsberg, Ind.Eng.Chem.(Anal.) 1943, 15, 576; 1944, 9, 1.



4:11-dibromofluoranthene-12-carboxylic acid (0.22g.) was boiled under reflux with 10% alcoholic potassium hydroxide (100 ml.) and 50:50 nickel-aluminium alloy (3.5g.) was added in 4 portions over 10 minutes. The mixture was boiled until all the aluminium had dissolved (1½ hours) and then for a further 1 hour. The mixture was filtered and the filtrate was diluted with water, acidified with hydrochloric acid, boiled, and cooled. Upon cooling, a very pale yellow solid was deposited and was filtered off, washed with water, and dried to give 0.12g.,m.p.265-281°. Crystallisation from acetic acid gave clusters of micro needles (0.05g.) m.p.278-282° (sublimed). A test for halogen was negative. The melting point of a sample of fluoranthene/

fluoranthene-11-carboxylic acid prepared by Campbell and Easton (loc.cit.) was determined as 284-289°, and was not depressed when admixed with the sample above. Recrystallisation of the debrominated acid gave m.p. 284-287°(0.02g.) which, once again, gave no melting point depression when admixed with fluoranthene-11-carboxylic acid. A sample was submitted for analysis but was lost in transit.

Yield = 0.05g. = 38% theoretical.

Esterification of the debromination product.

A sample of crude debromination product (0.19g.) was boiled under reflux with methanol (100 ml.) and concentrated sulphuric acid (3 ml.) for 24 hours. Most of the methanol was distilled off and the solution was poured into water to give a cream emulsion which eventually gave a pale yellow solid. This was extracted with benzene and the solution after distilling to low volume, was chromatographed on a column of alumina 8"x½" using a 50:50 mixture of benzene and light petroleum (80-100°) as developer. The single yellow band on the column moved quickly down the column and gave a pale yellow solid (0.18g.) m.p.71-81°. Crystallisation from methanol gave m.p. 85-88°. Recrystallisation from ethanol gave m.p.89-92°. Recrystallisation from methanol gave m.p.93-94.5°. A mixed melting point with methyl fluoranthene-11-carboxylate/

carboxylate (m.p.93-96°) gave no depression.

Analysis: Found: C,82.7%; H,5.3%.
$C_{18}H_{12}O_2$ requires: C,83.1%; H,4.7%.

The difficulty in purifying the ester was probably due to the fact that the debromination product was not purified.

Attempted mono-debromination of 4:11-dibromofluoranthene-12-carboxylic acid.

cf. Pursell (Thesis, Edinburgh).

Rule, Pursell, and Brown (J.1934, 168).

4:11-Dibromofluoranthene-12-carboxylic acid (0.24g.) was boiled under reflux with toluene (240 ml.) and copper bronze (0.24g.) for 6 hours. The copper was filtered off and extracted twice with boiling toluene, the entracts being added to the filtrate. The filtrate was distilled to low volume and, upon cooling, deposited the starting material (0.14g.) 306-308° (mixed m.p. satisfactory).

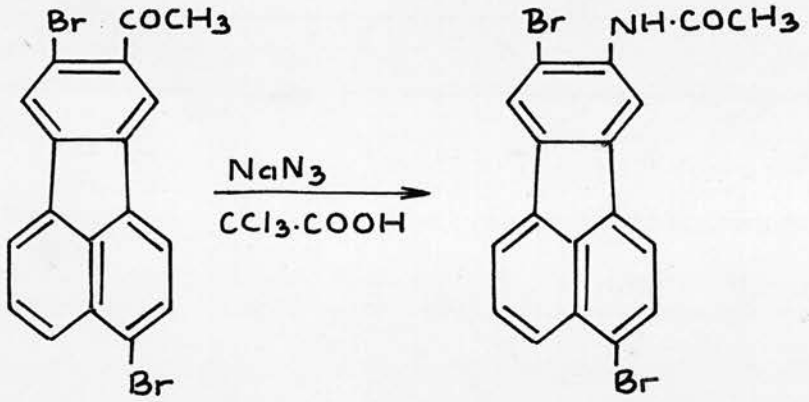
In another attempt, 4:11-dibromofluoranthene-12-carboxylic acid (0.20g.) was boiled under reflux with toluene (100 ml.) and copper bronze (0.7g.) for 50 hours. Once again, unchanged material (0.17g.) was recovered.

Pursell states that when debromination takes place the copper assumes a definite green colour. This change was not observed in the present experiments.

Preparation/

Preparation of 4:11-dibromo-12-acetamidofluoranthene by the Schmidt reaction.

cf. Dice and Smith, J.Org.Chem., 1949,14,179.



4:11-Dibromo-12-acetylfluoranthene (1.00g., 0.0025 mols) was dissolved in trichloroacetic acid (7g.) at 60° and powdered sodium azide (0.24g.,0.0037 mols.) was added in small quantities over ½ hour. After maintaining at 60° for 8 hours, with occasional shaking, nitrogen was no longer evolved and the mixture was poured into water and chopped ice to precipitate a yellow solid which was washed with water, then a little alcohol, and dried to give 1.01g. of product. The melting point of the latter was indefinite due to softening and sublimation but was approximately 250°. After boiling under reflux with alcohol (130 ml.), the undissolved solid (0.44g.) consisted of yellow needles, m.p.280-288°, (softened and sublimed below this). These were crystallised from glacial acetic acid to yield a felt of pale yellow needles/

needles (0.33g.), m.p. 284-288°, (darkened below this). A portion was recrystallised from glacial acetic acid to give m.p. 284-288° (darkened 281°).

Analysis:

Found: C,51.75%,H,2.7%,N,3.2%,Br,38.1%.
$C_{18}H_{11}NBr_2$ requires: C,51.95%;H,2.7%;N,3.35%.Br38.2%.

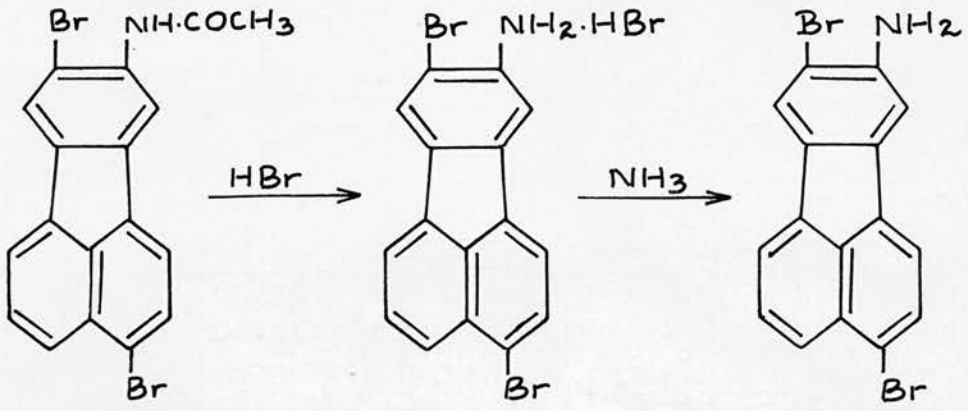
The alcohol extract, upon cooling, deposited a gelatinous precipitate (0.51g.) m.p.165-200°. Recrystallisation from glacial acetic acid gave a yellow solid (0.29g.), m.p. 175-220°.

Yield = 0.44g.= 43% theoretical.

Repeat of previous preparation.

In a repeat, using 2.27g. 4:11-dibromo-12-acetylfluoranthene, the crude product (2.29g.) was not boiled with alcohol but crystallised directly from glacial acetic acid (250 ml.) to give a felt of pale yellow needles (1.00g.) m.p. 280-284°.

Hydrolysis of 4:11-dibromo-12-acetamidofluoranthene.



4:11-Dibromo-12-acetamidofluoranthene (0.06g.) was boiled under reflux with constant boiling hydrobromic acid (10 ml.) for 3 hours. The solid did not dissolve but changed from a pale yellow to a cream colour/

colour and was filtered off, washed with constant boiling hydrobromic acid, then dry ether, and dried at 50° to give a cream solid (0.07g.), which sublimed at approximately 210° to dark yellow needles (possibly free amine) and decomposed at approximately 245-260°. The material was analysed for 4:11-dibromo-12-amino-fluoranthene hydrobromide as follows:-

Analysis: Found: Br,51.2%.
$C_{16}H_{10}NBr_3$ requires: Br,52.6%

Yield: = 0.07g. = 100% theoretical.

Liberation of 4:11-dibromo-12-aminofluoranthene from the hydrobromide.

When aqueous ammonia (20 ml.,0.880) was added to 4:11-dibromo-12-aminofluoranthene hydrobromide (0.20g.) the colour of the latter changed immediately from cream to deep yellow. The mixture was boiled for 1 hour, and the solid was filtered off, washed with water, then a little alcohol, and dried at 80° to give a deep yellow powder (0.16g.), m.p.256-258° (d)(sublimed at 180° to deep yellow elongated prisms and went brown at 248°). Crystallisation from benzene (40 ml.) gave golden yellow elongated prisms, m.p. 256-258° (d) (darkened 252°).

Analysis: Found:N,3.8%; Br,42.3%.
$C_{16}H_9NBr_2$ requires:N,3.7%; Br,42.6%.

Preparation/

Preparation of tribromofluoranthene.

Tobler et.al. (Helv.Chim.Acta, 1941,24,100E.)

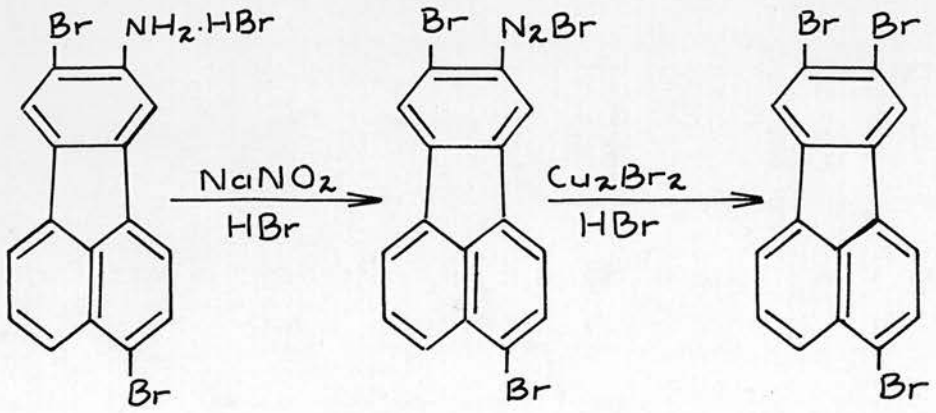
4:11-Dibromofluoranthene (70.0g.) and iodine (0.20g.) were heated at 90-95° in nitrobenzene (400 ml.) and bromine (10.5ml.) was dropped in over 4 hours whilst the mixture was stirred. After 20 hours stirring at 90-95°, air was blown in to remove hydrogen bromide and the mixture was cooled. The precipitate was filtered off, washed with nitrobenzene and alcohol and dried to give 67·7g. m.p. 170-182°. This crude product was recrystallised 4 times from nitrobenzene to give greenish-yellow needles having the following successive melting points:- 190-198°(52.4g.); 198-202°(47.5g.); 199-202°(44.4g.); 202-204°(40.3g.) (lit.205°).

Mixed m.p. with 4:11-dibromofluoranthene = 168-180°.

Yield = 40.3g. = 47% theoretical.

Attempted preparation of 4:11:12-tribromofluoranthene by the Sandmeyer reaction.

1st Attempt.



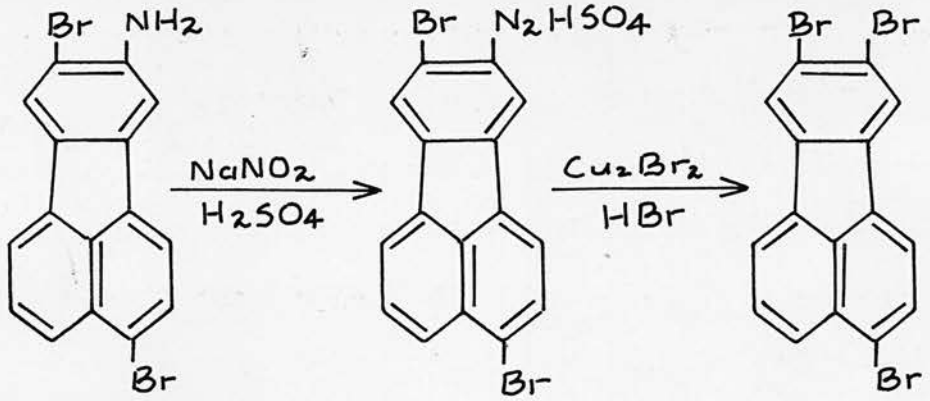
4:11-Dibromo-12-aminofluoranthene hydrobrom-

ide/

4:11-Dibromo-12-aminofluoranthene hydrobromide (0.90g.) was suspended in constant boiling hydrobromic acid (35 ml.) and diazotised at 0° with 20% aqueous sodium nitrite solution. The pale orange solid formed was insoluble even when water was added. The suspension was slowly added to freshly prepared cuprous bromide (0.32g.) in constant boiling hydrobromic acid (5ml.) at 0°, then heated to 60° over half an hour, diluted with water, and boiled to give a deep yellow solid (0.85g.). This was shown to be 4:11-dibromo-12-aminofluoranthene by its melting point and change of colour upon acidification.

2nd Attempt.

cf. Hodgson and Walker (J.,1933,1620).



A solution of sodium nitrite in concentrated sulphuric acid (1g./7ml.) was prepared by adding the powdered nitrite to the cooled acid with vigorous stirring/

stirring and increasing the temperature to 70° to dissolve the nitrite solution. The solution was cooled and filtered from sodium bisulphate.

4:11-dibromo-12-aminofluoranthene (0.90g.) was boiled with glacial acetic acid (12 ml.) but was only slightly soluble. The suspension was cooled to 15° and added slowly, with stirring, into the sodium nitrite solution (5 ml.= 400% excess) keeping the temperature below 20°. Any lumps were broken up and the mixture was allowed to stand for 1 hour to give a light brown powder in a dark brown solution, which gave a red non-flocculent precipitate with alkaline β-naphthol solution. The suspension was stirred slowly into freshly prepared cuprous bromide (1.5g.) in constant boiling hydrobromic acid (20 ml.) keeping the temperature below 20°, and the suspension formed was left over ½ hour, warmed to 60° over ½ hour and maintained at this temperature for 10 minutes, heated to 95°, and finally diluted with water (300 ml.) and boiled. The orange suspension was filtered off, washed with water, and dried to give 1.06g., m.p.125-165°. This crude product was dissolved in chlorobenzene and chromatographed on a column of alumina 20"x11/16" using chlorobenzene as developer. A uniform very pale yellow band (uniform dull green under U.V.light) was readily eluted to leave some dark brown material/

material at the top of the column. The product from the pale yellow band was found difficult to purify by crystallisation and so was rechromatographed on a column of alumina 15"x½", using benzene as solvent and a 50:50 mixture of benzene and light petroleum (80-100°) as developer.

Fraction 1. The solution from the lower part of the column was boiled to low volume and poured into alcohol to precipitate a pale yellow, non-crystalline solid (0.09g.) m.p. 91-151°. The mother liquors gave 0.05g., mp. 125-171°.

Fraction 2. Similar treatment of the solution from the upper part of the column precipitated 0.25g., m.p. 125-160° and the mother liquors gave 0.06g.,m.p.105-167°.

Crystallisation from acetic acid of the 0.25g. of m.p. 125-160° gave m.p. 148-168° (0.12g.) and recrystallisation gave m.p. 155-182°(0.07g.)

Analysis:

Found: Br,57.7%.
$C_{16}H_7Br_3$ requires: Br,54.6%.
$C_{16}H_6Br_4$ requires: Br,61.7%

All remaining solids from fractions 1 and 2 were bulked together and crystallised from nitrobenzene. The solution had to stand overnight before any solid (0.01g.) was deposited and this had m.p. 182-192° (softened below this and a very few crystals did not melt until 235°). The mother liquors, upon further standing,/

standing, deposited fine pale yellow needles (0.02g.), m.p. 190-207° (a few crystals did not melt until 213°) which were analysed as follows:-

Analysis: Found: Br, 59.1%.
$C_{16}H_7Br_3$ requires: Br, 54.6%.
$C_{16}H_6Br_4$ requires: Br, 61.8%.

3rd Attempt.

4:11-Dibromo-12-aminofluoranthene (0.68g.) was added in small portions to a solution of sodium nitrite in concentrated sulphuric acid and (5 ml.) keeping the temperature below 15°. The suspension was left for ½ hour at 15° and then added to freshly prepared cuprous bromide (1.5g.) in constant boiling hydrobromic acid (10 ml.) keeping the temperature below 15°. The suspension formed was maintained at 15° for ½ hour, heated to 60° over 20 minutes, diluted with water, and boiled. The orange suspension was filtered off, washed with water, and dried to give 0.90g. The crude product was dissolved in benzene and chromatographed on a column of alumina 21"x11/16", developing with a 50:50 mixture of benzene and light petroleum (80-100°). The appearance of the developed column was the same as in the previous experiment and the following materials were obtained when the fractions were distilled to dryness:-

1. Bottom of main zone gave pale yellow needles (0.34g.) m.p. 170-215°.

2/

2. Top of main zone gave pale yellow needles (0.26g.) m.p. 187-230°.

Both fractions were combined and rechromatographed on a column of alumina 20"x11/16" using the same conditions as before. The following materials were obtained:-

1. Lower region gave 0.20g., m.p. 162-206°. This material was rechromatographed on a column 26"x$\frac{3}{4}$" to give the following fractions:-

(a)Bottom.m.p. 154-203°. (b)Middle.m.p.163-210°.
(c)Top. m.p. 164-206°.

(a), (b) and (c) were combined and crystallised from nitrobenzene to give m.p. 205-220°. Recrystallisation gave m.p. 215-227°.

2. Middle region gave 0.29g.,m.p.158-206°. Repeated recrystallisations from nitrobenzene gave the following successive melting points:- 215-225°(0.12g.); 218-225°(0.09g.); 222-228° (0.07g.); 223-228°(0.05g.). The mother liquors from the final recrystallisation gave 0.004g., m.p.224-228°. All materials from nitrobenzene consisted of pale yellow needles.

The 0.05g.,m.p.223-228°, were crystallised from benzene to give m.p. 223-228° and submitted for analysis.

Analysis:

Found:	C,36.7%;	H,1.4%;	Br,61.6%
$C_{16}H_7Br_3$ requires:	C,43.8%;	H,1.6%;	Br,54.6%.
$C_{16}H_6Br_4$ requires:	C,37.1%;	H,1.2%;	Br,61.7%.

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The material lost its fine crystalline appearance when crystallised from benzene but sublimed at approx. 160° to give needles.

3. Top region gave 0.05g., m.p. 190-245°(upper limit was only a few crystals) Crystallisation from nitrobenzene gave m.p. 210-245° (0.04g.).

Analysis:

Found: Br, 61.6%.
$C_{16}H_7Br_3$ requires: Br, 54.6%.
$C_{16}H_6Br_4$ requires: Br, 61.7%.

Conclusion: When subjected to the Sandmeyer reaction, 4:11-dibromo-12-aminofluoranthene gave a mixture of tri- and tetra-bromofluoranthene. The tetrabromofluoranthene probably resulted from the direct bromination of the tribromofluoranthene originally formed. Bromination probably occurred with free bromine provided by the reaction between concentrated sulphuric acid and hydrobromic acid.

SUMMARY.

1. The products of the action of acetyl bromide on fluoranthene in the presence of aluminium chloride were 4- acetylfluoranthene, 11- acetylfluoranthene and 4:12 diacetylfluoranthene.

2. The identities of the mono-acetylfluoranthenes were shown by their conversion to the corresponding acetamidofluoranthenes by the Schmidt reaction.

3. The orientation of 11- acetylfluoranthene was confirmed by its oxidation to 11-fluoranthene carboxylic acid.

4. Diacetylfluoranthene was orientated by oxidising it and showing the resulting fluoranthene dicarboxylic acid to be different from fluoranthene -4:11- dicarboxylic acid although identical with the acid obtained from fluoranthene and oxalyl chloride under Friedel - Crafts conditions (Campbell and Easton, J., 1949, 340).

5. Decarboxylation experiments were performed with fluoranthene carboxylic acids.

6. The orientation of 4:12- diacetylfluoranthene was confirmed by its conversion to diacetamidofluoranthene by the Schmidt reaction. Hydrolysis followed by diazotisation and the Sandmeyer reaction gave a dibromofluoranthene which was different from 4:11- dibromofluoranthene.

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7. The preparation of ethylfluoranthenes by the reduction of acetylfluoranthenes was unsuccessful.

8. 4:11- Dibromofluoranthene and acetyl bromide in the presence of aluminium chloride gave 4:11- dibromo -12- acetylfluoranthene, orientated by oxidation to a dibromofluoranthene carboxylic acid which gave fluoranthene -11- carboxylic acid when debrominated.

9. 4:11- Dibromo -12- acetylfluoranthene was converted to 4:11- dibromo -12- aminofluoranthene by the Schmidt reaction followed by hydrolysis. An attempt was made to convert this amine to 4:11:12- tribromofluoranthene by diazotisation and the Sandmeyer reaction but the main product was a tetrabromofluoranthene.

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